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by

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I. Introduction

Bulk silicon is an indirect band gap material. When carriers are injected into bulk silicon, electron-hole recombination takes place thermally via phonon exchange, and not by emission of photons. Porous silicon, on the other hand, is a fairly efficient emitter of light in the visible region. Much research is currently under way to find out what makes porous silicon able to emit light. One main theory suggests that the energy bands of bulk silicon may be "squeezed" by being quantum confined, and porous silicon is just an array of quantum silicon wires. Another possibility is that defects in the huge surface area of porous silicon create additional energy bands. These defect energy bands would allow carrier recombination to take place via photon emission. Porous silicon would be very useful as an optically active material. It is compatible with existing silicon electronics and is not expensive to make. The possibility of having all-silicon electrooptic technology puts porous silicon at the focus of much research.

Many photoconductive studies have been done on porous silicon. The purpose of this project was to do preliminary electroreflectance and electroabsorptive studies of porous silicon. Electroabsorption studies on porous silicon have not been previously reported, and the technique can reveal much information about the energy band structure and composition of porous silicon.

II. The Electroabsorption Measurement

An electroabsorption measurement records the change in the amount of light absorbed by a material, as a function of wavelength, when a DC electric field is applied across it. As shown in Figure 1, at any particular wavelength the sample absorbs a constant fraction of the incident light intensity with time when no electric field is applied across the sample. When an electric field is applied, the sample absorbs a different, but still constant, amount of light. This change in absorption, which is the electroabsorption signal we were interested in, is only about one percent at the most. It is too small to find by just measuring the absorption with the field on and with the field off and taking the difference. The huge DC absorption signal would overload the detector before it could see the tiny AC signal of interest, the change in absorption.

For this reason, a Stanford Research 530 Lock-In Amplifier was
used to detect only signals at the same frequency as the applied field, which was used as a reference signal. This is why the applied field was a square wave instead of an actual DC signal, but hopefully the field redistribution time

in porous silicon is much longer than the period of the applied field so that the field appears to the sample to be DC[1].

An electroreflectance measurement is similar to an electroabsorption measurement, except that it records the change in the sample's reflectance when an electric field is applied. This type of measurement was tried at first, since the samples were easier to make because the porous film did not have to be lifted off the bulk Si substrate.

For both types of measurement, a tungsten filament was used as a broadband light source with a SPEX 1681 0.22 m Spectrometer to select a narrow wavelength band to scan along the spectrum. A silicon PIN detector was used to gather the light transmitted by the sample, and a lock-in amplifier picked out the electroabsorption signal. The data was recorded with a program written in C by Michael Estes. In order to normalize the electroabsorption signal to the response of the detector and the tungsten lamp's emission spectrum, we looked at the fractional change in absorption. We divided the electroabsorption signal by the absorption signal with no field applied, so that the non-linear detector response and lamp emissions would be canceled.
For electroreflectance measurements, the setup was the same except that the incident light reflected off the sample to the detector, rather than passing through the sample.

III. Sample Preparation

This study concentrated on thin films of porous crystalline silicon. Lee Hirsch made the samples using an anodic etch. As shown in Figure 3, a small area of a bulk crystalline silicon wafer was sealed off with an O-ring, and that area was etched in a container of ethanilic hydrofluoric acid (HF:H₂O:EtOH), with current running through the wafer. The etching process lasted from five minutes to thirty minutes, depending on the desired thickness of the film. The acid concentration was anywhere from sixteen percent to twenty-five percent, and the etching current ranged from five to twenty milliamps per square centimeter for a particular sample. Weaker acid concentrations and higher current densities lead to larger pores in the resulting porous layer. The pores in porous silicon usually vary from about one to ten nanometers in width.

The etching takes place at the bottom of the pores since current only runs through the bulk Si wafer and not up the porous "fingers." In this way a free-standing film of porous silicon, for use in electroabsorption measurements, is created by changing the acid concentration to five percent and increasing the current density to one hundred milliamps or more. This effectively creates one huge pore across the entire bottom of the porous layer, detaching it from the bulk Si substrate and causing it to float up to the top of the solution, where it is placed on a piece of glass. For electroreflectance measurements, the porous layer is not detached from the bulk Si substrate. The junction between the porous film and the substrate reflects light back through the porous silicon and then to the detector.
A sandwich electrode configuration, shown in Figure 4, was used throughout this experiment. For electroabsorption measurements, the porous silicon film was lifted off the bulk Si substrate and positioned between two glass plates with layers of Indium Tin Oxide (ITO) on one side. The plates were aligned and cemented together with UV-cure epoxy so that the ITO layers did not touch. In this way an electric field could be applied across the porous silicon layer without actually running a substantial amount of current through it.

For electroreflectance measurements, an insulating layer of polymethyl methacrylate (PMMA, a transparent plastic) and an approximately fifty percent transmissive chromium layer were deposited on top of the porous silicon layer. The chromium acted as one electrode and the bulk Si substrate as the other. As shown in Figure 5, this was also a sandwich electrode configuration.

Electroreflectance measurements were not successful but are discussed briefly here. As shown in Figure 6, the fractional change in reflectance with applied field is very small, about one one-hundredth of one percent at most.
It is unclear whether or not the peak at 3.5 eV is from the direct band gap of bulk silicon. It may be an artifact due to the tungsten lamp's emissions and the detector's sensitivity both trailing off at that point. The remainder of the ΔR/R spectrum is very flat.

Another problem was that the signal had a large amount of AC coupled noise. It was difficult to measure exactly how much noise there was in order to subtract it, since it changed with time depending on what other equipment was running nearby. If the wrong amount of noise were subtracted from the original signal, the normalization step would cause ΔR/R to have a false curve up at each end. This could also be the source of the peaks in Figure 6.

The main reason the signal is so weak is likely that most of the incident light reflected off the top (chromium) surface of the sample and was never modulated by the porous silicon. Only a small portion of the incident light actually passed through the chromium, PMMA, and porous silicon layers and was modulated and reflected out again. The use of a chromium layer could not be avoided since all attempts at a transparent front electrode yielded huge interference fringes modulating the signal. We decided that electroabsorption measurements were more promising.

V. Photoluminescence Measurements

As a preliminary step to electroabsorption measurements, we took photoluminescence (PL) spectra of the samples. Porous silicon films with stronger PL presumably have more of the characteristics we want to explore. The stronger the PL of the sample, the less like bulk silicon it must be.

For the photoluminescence measurements, the porous silicon film was excited with 365 nm light from a mercury arc lamp. Two porous silicon films had especially strong PL signals. The first, #1807-1, was etched for fifteen minutes in twenty-five percent HF (HF:H₂O:EtOH in the ratio 1:1:2) with a current density of five mA/cm². It was lifted off with a one hundred second etch in five percent HF with one hundred mA/cm² current density. Its PL is the strongest, peaking at about fifty-eight picowatts per nanometer at about 1.8 eV (689 nm). This sample also had the strongest electroabsorption signals.
The other sample, #1307-10, etched for five minutes in sixteen percent HF (HF:H₂O:EtOH in the ratio 1:1:4.25) with ten mA/cm² current density. The lift-off conditions were similar to those for sample #1807-1. The photoluminescence from #1307-10 is only about one-third as strong as that from #1807-1, and its electroabsorptive signal is not as good. PL measurements were helpful in determining which samples were of further interest. It was assumed that if a sample did not have the right composition to give off light very efficiently, it did not have the characteristics of porous silicon that we wanted to explore.

VI. Electroabsorption Measurements

When sizable free-standing porous silicon films were obtained that also had strong photoluminescence signals, they were mostly made from p-type (about 1-20 Ω·cm resistivity) bulk silicon wafers. The films made from p+-type (about 0.001-0.02 Ω·cm) wafers were easier to lift off but did not have strong PL signals. The top and bottom of a porous silicon film may be quite different. One side may be more polished or have smaller pores than the other because the beginning and end of the etching process are not the same. This means the contact areas with the ITO electrodes could be quite different. Then when a voltage is applied across the porous silicon film, depletion regions formed at the porous silicon-ITO junctions would not be the same. Most of the voltage could be dropped across one side of the sample. The electroabsorption signal would then depend strongly on the polarity of the
applied field. A graph of the sample's dark current vs. voltage characteristics shows whether one side of the sample is very different from the other. This measurement was made with a Keithley 617 Programmable Electrometer. Figure 9 shows a reasonably small difference in current with different applied voltage polarities for sample #1807-1. This difference is explored in the electroabsorption measurements, but the electrode contacts were considered sufficient for our purposes. Also, the current through the sample is small enough that it is possible to speak of a large field applied across the sample, not just a current running through it. Because of this we were confident that we had a good sample configuration for electroabsorption measurements.

Figure 9. Current vs. voltage characteristics of sample #1807-1.

Sample #1307-10 does not have a very useful electroabsorption signal for our purposes. The sample is so thin and smooth that large interference fringes modulate the electroabsorption signal. This is shown in Figure 10. The fringes are probably from a slight change in the index of refraction of the porous silicon when the field is applied. There are really two sets of interference fringes, one when the field is on and one when the field is off. The fringe pattern visible in the electroabsorption signal is the difference between the two static fringe patterns. It is unclear which part of the fringe envelope is the desired electroabsorption signal. It could be the actual envelope or some average of the envelope. Other samples do not have this characteristic and are more useful.

Sample #1807-1 is thicker and rougher than the previous sample, #1307-10. Its electroabsorption signal does not have interference fringes. On the following pages, $\Delta T/T$ for porous silicon film #1807-1 is shown as a function of applied voltage with a 1kHz square wave applied. $\Delta T/T$ for #1807-1 is also shown as a function of the frequency of the applied field, with 100 V field amplitude. All fields were applied with the same polarity. The
signals are first shown separated into components in phase with and ninety
degrees out of phase with a signal 95.6° from the applied field. This is to show
where the signal is positive and where it is negative. The total signal magnitudes
are shown separately. The phases of the signals, Figure 17, are not constant, so
the total ΔT/T signal magnitude is shown as always positive.

In Figure 13, several features are visible in the ΔT/T spectrum. Peaks in
the electroabsorption signal are expected at band gap edges. The large peak at 1.2
eV nearly corresponds to the (1.1 eV) indirect band gap of bulk crystalline
silicon. This looks like the Franz-Keldysh effect[2] in bulk silicon because the oscillations in ΔT/T vary with
applied voltage[3]. The smaller peak at 3.5 eV corresponds to the direct band gap
of bulk silicon.

There are a couple of possible reasons why we see nothing in these
electroabsorption spectra that can't be explained by bulk silicon. One may be
that porous silicon really is just small bulk silicon with many radiative surface
states. That would not account for the fact that this sample emits light. Another possibility is that there really
are many other features in the ΔT/T spectrum, but they are washed out because we observed a relatively large
area of the sample. The size of the porous silicon "islands" varies widely. The smaller chunks are less likely to
have surface defect states that would allow carriers to recombine non-
radiatively. It appears that an electroabsorption measurement is more sensitive to the larger porous silicon
pieces, since there are more of those, and any signal from the smaller pieces of interest is washed out.

The ΔT/T signal also increases in magnitude with decreasing applied field
frequency, as shown in Figure 16. This is because the capacitance of the sample prevents the field from having time to
settle down to being entirely on or entirely off before the next period begins. Lower frequency fields have
periods longer than the time required for the field to "relax" in the material, and the difference between the field on
and field off states is greater. This gives a stronger electroabsorption signal, as shown. Additional evidence for this is
that ΔT/T becomes more in phase with the applied field at lower frequencies,
and is nearly 90° out of phase with the applied field at higher frequencies.
(Keep in mind that the signal phases are relative to 95.6° from the applied field,
not relative to the applied field as 0°
phase itself.) This suggests a time constant effect as well.

The jumps in phase, as shown in
Figure 17, occur at the minima of the
ΔT/T signals. The phase changes cannot
be explained by optical interference since the spacing between phase jumps
increases for shorter wavelengths. At this time the cause of the phase changes
is not clear. It is a very interesting effect
and needs further study.
Figure 11. In phase $\Delta T/T$ from #1807-1 at several voltages.

Figure 12. Quadrature of $\Delta T/T$ from #1807-1 at several voltages.
Figure 13. $\Delta T/T$ from #1807-1 at several voltages.

Figure 14. In phase $\Delta T/T$ from #1807-1 at several frequencies.
Figure 15. Quadrature of $\Delta T/T$ from #1807-1 at several frequencies.

Figure 16. $\Delta T/T$ from #1807-1 at several frequencies.
VII. Conclusions

We were successful in getting a electroabsorption signals from porous silicon. Unfortunately, this came at the end of the summer and the session ended while further research was still necessary. The voltage dependence needs to be explored further to make certain it can be fully explained by the Franz-Keldysh effect. The phase shifts contain much information that needs to be deciphered. The changes in the electroabsorption signals when the polarity of the field is reversed have only been looked at briefly. Also, the effect of making the porous silicon from different types of bulk Si wafers (p-type, p+-type, n-type, with varying dopants and resistivities) needs further attention. Electroabsorption studies of porous silicon have only just begun, but this project shows the technique works and there is a wealth of information to gain from it.

VIII. References