29 Jan 1993

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Gregory J. Teets

USING MODULATED BEAM MASS SPECTROMETRY TECHNIQUES TO DETERMINE HYDROGEN LEVELS IN SINGLE CRYSTAL AND ETCHED SINGLE CRYSTAL SILICON

Gregory J. Teets*
Department of Nuclear Engineering

ABSTRACT

Silicon is an important element that has many applications ranging from semiconductors to solar cells. The quantity, diffusion, and bonding of hydrogen atoms in the silicon can play an important role in the electrical characteristics of single crystal and etched single crystal silicon. The hydrogen bonds to the impurities and to the dangling bonds in the silicon and reduces current leakage and improves performance [1-4]. Until now hydrogen bonding data has been extrapolated from related studies to determine hydrogen evolution temperatures from the silicon. Abrefah, Olander, et al. [1] studied deuterium evolution from silicon where the deuterium had been implanted at 1.7 - 9.2 atmospheres. Pankove and Lampert [2] estimated that H_2 evolution began at 350 °C and ended at 550 °C. None of these papers studied hydrogen (H_2) using modulated beam mass spectrometry to obtain exact information on how hydrogen release rates, temperature, and time are related. This paper will describe the use of modulated beam mass spectrometry techniques to determine thermodynamic properties of hydrogen in silicon.

INTRODUCTION

The study of hydrogen in silicon is an important one. When hydrogen is introduced into silicon, it attaches to dangling silicon bonds and impurities and passivates them [2]. It has been found that silicon chips manufactured from crystalline silicon that was exposed to hydrogen were more reliable and had a longer life [1]. A better understanding of the bonding and diffusion of hydrogen in silicon would enable beneficial control of the placement and quantity of the hydrogen in silicon.

Past experiments on hydrogen in silicon have used methods other than modulated beam mass spectrometry. Pankove et al. [2] heated silicon and monitored the change of the pressure in a vacuum system to estimate the hydrogen evolution temperature. Abrefah, Olander, et al. [1] used a modulated beam mass spectrometer but substituted deuterium or tritium for hydrogen. Other studies

*Current affiliation - Department of Engineering Management

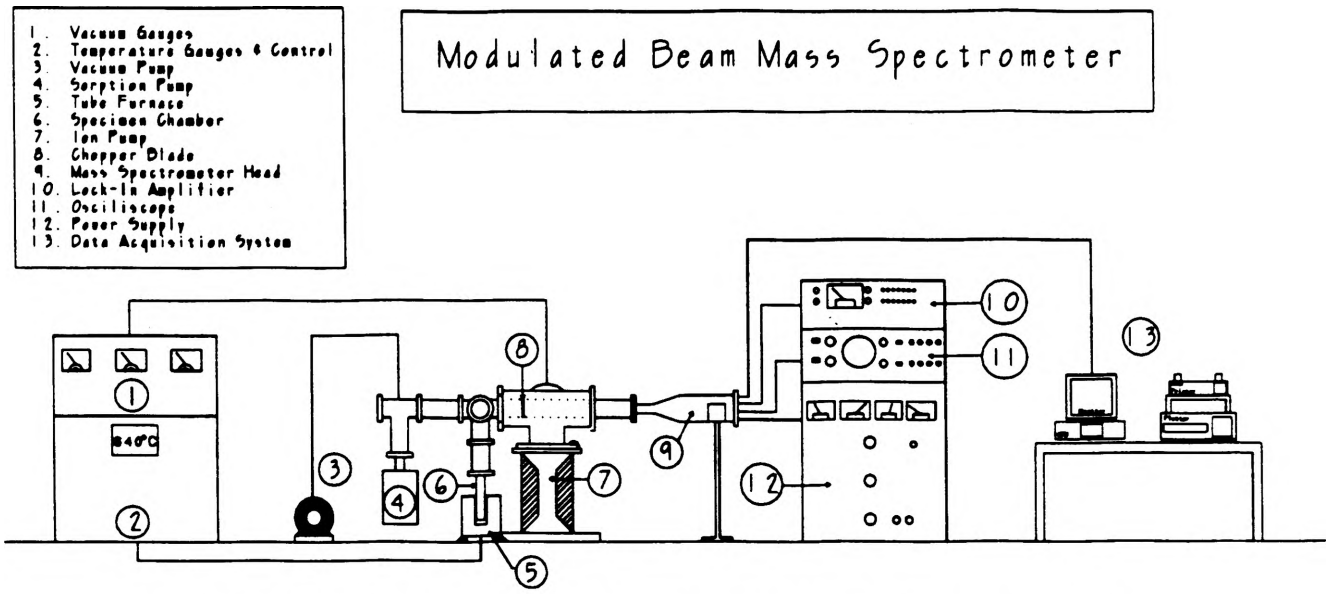

Figure 1: The Modulated Beam Mass Spectrometer at UMR

have used low temperature data and extrapolated it to higher temperatures.

There are three distinct advantages to using the modulated beam mass spectrometry technique used in this experiment. First, it allows us to measure hydrogen diffusion directly; substitution with deuterium or tritium is not required. Second, the modulated beam mass spectrometer measures hydrogen release rates in real time. As the hydrogen is released, the data is measured and recorded, allowing valuable time, temperature, and release rate correlations to be recognized. Third, the test is not destructive, provided temperatures are low enough to do no damage.

EXPERIMENTAL PROCEDURE

The modulated beam mass spectrometer (MBMS) was designed and built by Dr. A. Kumar and his students at the Materials Research Center at UMR [5]. Figure 1 shows a diagram of the MBMS system. The technique involves heating specimens in a high vacuum to drive off the hydrogen (and other gases) and measuring it with a quadrupole mass spectrometer using a modulated beam. The system operates in real time providing time and temperature dependent hydrogen evolution rates that allows differentiation between various forms of bound hydrogen. The modulated beam technique permits the determination of hydrogen evolution rates in real time and the system's extraordinary sensitivity (tenths of a nanogram per second) allows the analysis without resorting to the use of hydrogen isotopes such as deuterium.

The sample is heated in a platinum lined stainless steel chamber. The platinum lining is necessary to prevent the interaction of either the hydrogen from the sample or the sample itself with the specimen chamber. All of the system's

components, except the vacuum seals, are constructed of stainless steel.

Modulated beam mass spectrometry uses a modulated beam and a lock-in amplifier to improve sensitivity over that of a conventional mass spectrometer. The hydrogen flow evolved from the specimen is given periodicity by a fixed frequency, two-bladed chopper. The flow is directed into the ionizer of the mass spectrometer (EAI Quad 250) located in the vacuum system. Using the lock-in amplifier, only the modulated beam is detected. The hydrogen flow rate is converted into a voltage signal by the mass spectrometer. This time dependent signal is sent to the data acquisition computer where it is recorded.

The hydrogen flow rate is proportional to the voltage signal from the mass spectrometer. Before each experiment, the system is calibrated using a hydrogen calibration gas. Hydrogen is leaked into the system at a controlled rate. By recording the mass spectrometer signal due to this known flow, absolute calibration of the mass spectrometer is accomplished [5].

The temperature of the experiment is controlled by a separate computer using a thermocouple located outside the specimen chamber. The temperature of the sample is monitored by a thermocouple inside the chamber. The temperature control system provides for increasing the temperature of the sample at a constant rate (ramp) and/or maintaining the temperature at a preset value. Temperature readings of the sample along with the mass spectrometer signal are sent to the data acquisition computer at desired time intervals for recording.

The data acquisition computer consists of an IBM PC, a data acquisition board, and software. The data acquisition computer displays the information in several ways. It continuously displays data (millivolt readings, temperatures, etc.) on the screen and outputs it to a strip chart plotter. At desired time intervals, the data acquisition computer digitally records the mass spectrometer data onto the hard disk and onto an IBM Proprinter. The data is analyzed using software developed at UMR by Dr. Kumar's students.

Measurement of Hydrogen Release

Prior to insertion into the specimen chamber of the MBMS system, the silicon samples were thoroughly cleaned. First, they were gently rinsed with acetone to remove dirt and oil deposits caused by handling. Next, the silicon samples were rinsed with methyl alcohol to remove any residues left by the acetone rinse.

After weighing and measuring the dimensions, the specimen is inserted into the platinum lined specimen chamber. The mass spectrometer was turned on, calibrated, and the settings recorded using the procedure described above. Next, the temperature control system was programmed and the tube furnace was placed around the specimen chamber. The data acquisition hardware and software were activated and the control parameters set. When the furnace is activated the data acquisition system takes its first reading. From now until the end of the run, the data acquisition hardware and software will monitor and record the voltage signals from the mass spectrometer at a preset interval.

After a given time period or when the system returns to equilibrium, the data acquisition system and the furnace are shut down. The tube furnace was removed and the specimen chamber was allowed to cool. After sufficient cooling, the specimen was removed from the chamber. The specimen was weighed and measured again and put into storage for future reference.

Data Interpretation and Manipulation

After the experiment, the mass spectrometer data from the data acquisition computer (which is saved as a Lotus file) is imported into a spreadsheet package. The spreadsheet package allows more complex manipulations of the data than does the data acquisition software. The millivolt readings are converted to flow rates using the following formula:

$$\frac{\text{Mass Spectrometer reading (mV)} \bullet \text{Calibrated Flow (ng/s)}}{\text{Calibrated Signal} \bullet \text{Lock-in Sensitivity} \bullet \text{Sample weight}} \qquad (1)$$

To make the hydrogen measurements more accurate, the background signal is subtracted off. If necessary, the data is averaged to smooth out the curves. The temperature rates, hydrogen flow, and time are plotted as shown in the Figures 3 through 6.

RESULTS AND DISCUSSION

Four experiments were performed for this paper. The first used an unetched silicon single crystal to serve as the base for comparison. The second experiment was on an etched silicon sample. To be sure that the hydrogen background from the sample tube was negligible compared to the normal hydrogen background of the system, two experiments were done on the empty specimen chamber at two different temperature ramp rates.

Unetched Silicon Single Crystal

The MBMS system was used to determine the quantity of hydrogen in an unetched silicon single crystal. This sample was used as the base case for comparison. This sample was washed and placed in the specimen chamber as described. The MBMS system was calibrated and the control systems set. The sample was heated at a 10 °C per minute ramp to final temperature of 940 °C where it was held until the

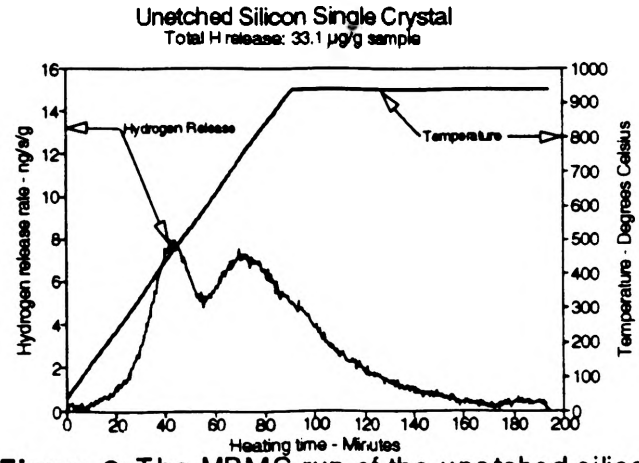

Figure 2: The MBMS run of the unetched silicon

system returned to equilibrium. A plot of this run is shown in Figure 2.

The first peak on the hydrogen release curve occurred at 470 °C. The peak was followed by a valley which occurred approximately 15 minutes after the first peak. At approximately 760 °C a second peak occurred. After the second peak, the hydrogen release rate gradually dropped back to system background. The total amount of hydrogen released from this specimen was 33.1 µg per gram of sample.

Etched Silicon Single Crystal

A silicon single crystal was etched with at 12.5% solution of hydrofluoric acid. The etching procedure created a small zone of amorphous (non-crystalline) silicon. The same basic procedure was used for the etched silicon single crystal as was used for the unetched silicon. To provide more information, the temperature ramp rate was changed to 4 °C per minute with a final temperature of 540 °C. A plot of this run is shown in Figure 3.

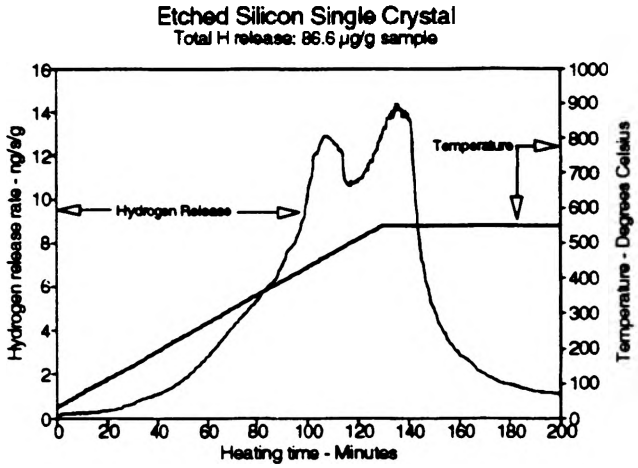

Figure 3: The MBMS run of the etched silicon

As was the case with the unetched sample, the first peak occurred at approximately 470 °C. The first peak was followed by a valley and a second peak. The temperature at which the second peak occurred was 540 °C, the dwell temperature. The second peak abruptly dropped off to system background. The total amount of hydrogen evolved from the etched specimen was 86.6 µg per gram of sample.

Empty Tube Analysis

To help verify the results and assure that the background signal from the specimen chamber was negligible, an analysis was done on the empty specimen chamber. To verify the unetched silicon data the empty chamber was analyzed by heating it to 840 °C at a rate of 7 °C per minute. The chamber was held at 840 °C for several hours. To verify the etched silicon data the specimen chamber was heated at 4 °C per minute to a final temperature of 640 °C where it stayed for several hours.

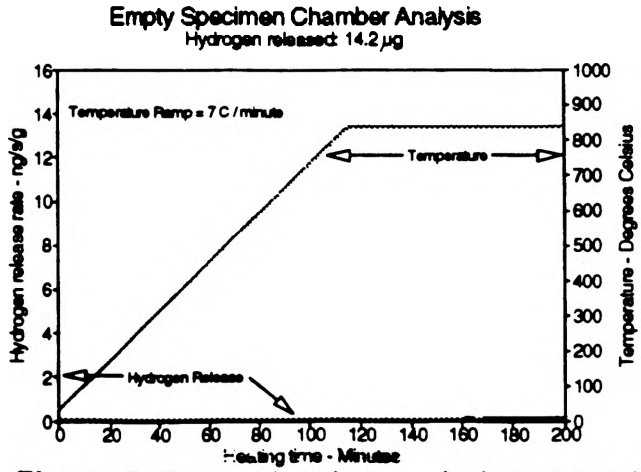

Figure 4: Empty chamber analysis to 840 °C

The results of these experiments can be seen in Figures 4 and 5, respectively. From these experiments it was determined that the hydrogen evolution from the empty stainless steel tube was negligible when compared to the normal hydrogen background of the MBMS system.

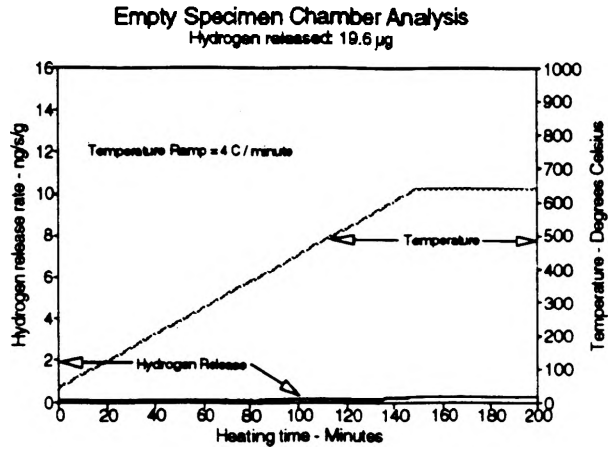

Figure 5: Empty chamber analysis to 640 °C

CONCLUSIONS

It was hypothesized, by Srikanth and Ashok [6], that molecular hydrogen (H_2) is basically immobile in silicon at temperatures lower that 500 °C and that hydrogen bonded to dangling silicon bonds break above 500 °C . This investigation confirms that hypothesis. If lines are drawn from the peaks of the release rate curves, it is found that the first peak occurs at 470 °C (see Figures 6 and 7). Despite the fact that the two experiments used two different temperature ramp rates (4 °C per minute and 10 °C per minute), the first peak occurs at the same temperature. Because this peak occurs at the same temperature in both experiments, we can conclude that the release rate of the hydrogen is independent of the temperature ramp rate. Therefore, we can attribute the release of the hydrogen to be a thermodynamic property rather than a kinetic property of the hydrogen in the silicon. If it were a kinetic property, the hydrogen evolution rate would increase with the increased temperature ramp rate. In these experiments that did not happen.

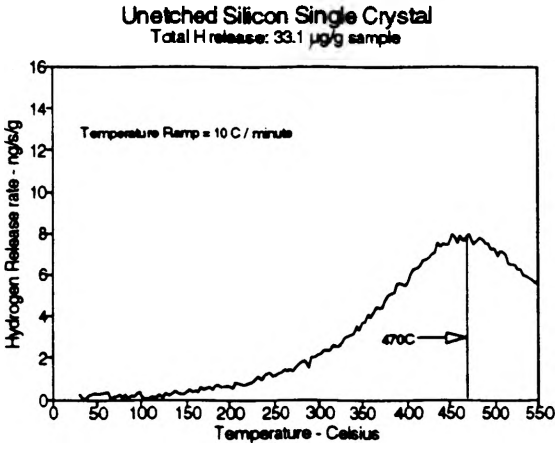

Figure 6: Unetched silicon, 1 st peak at 470 °C

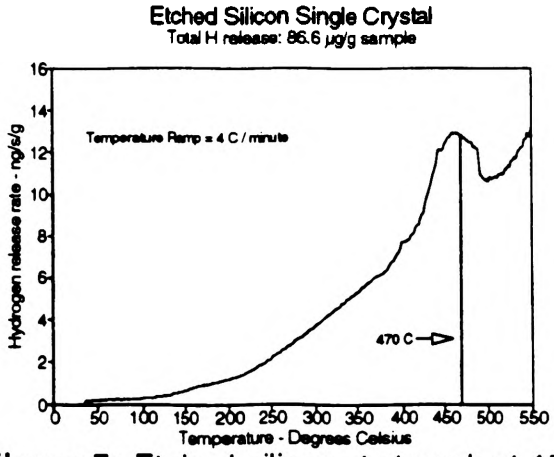

Figure 7: Etched silicon, 1 st peak at 470 °C

The hydrogen release that causes the second peak needs further investigation. It occurred at two different temperatures in the two experiments. In the experiment involving the etched silicon single crystal, the peak dropped off rapidly when the temperature increase ended. More experiments with higher tempera-

tures and different temperature ramp rates need to be performed.

Quantitatively, it was found that the etched silicon contained more hydrogen than the unetched silicon specimen. The amorphous silicon found in the etched sample contains more dangling bonds. Since the etched silicon contains more amorphous silicon, which is the source of the dangling bonds and therefore the hydrogen, there is more hydrogen to be released.

Another interesting feature of the release rate curves is that the second hydrogen release rate peak occurs about 30 minutes after the first peak (see Figures 2 and 3). This could be explained by the time required for the bulk hydrogen to travel through the crystal lattice before release. This aspect, too, needs further investigation.

SUMMARY

Modulated beam mass spectrometry has been used to investigate the properties of hydrogen occupancy and diffusion in silicon. It has been found that heated silicon evolves hydrogen with two characteristic peaks. The first peak occurring at approximately 470 °C with a second peak occurring 30 minutes later. It was also found that etched silicon single crystal contains about 3 times as much hydrogen than does unetched silicon single crystal.

ACKNOWLEDGMENTS

The author would like to thank Mr. Mark Geissler for his help in learning how to use the MBMS, Dr. Brent Heuser, University of Missouri-Columbia Research Reactor, for providing the silicon specimens, and Dr. Allan Pringle, Department of Physics at UMR, for his helpful discussions about silicon. Most of all, I would like thank faculty advisor, Dr. Arvind Kumar, for his help, support, and encouragement during this project.

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