

Elastic Properties of Thin Film Silicon

Final Report
1 June 1999–23 August 2002

R.O. Pohl
Cornell University
Ithaca, New York



NREL

National Renewable Energy Laboratory

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Golden, Colorado 80401-3393

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NREL Technical Monitor: R. Matson

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Elastic Properties of Thin Film Silicon

R.O. Pohl, Cornell University
NREL Grant #: AAD-9-18668-12

Final Report

Introduction

The original purpose of this research, as stated in the annual reports, was the study of the role of hydrogen in thin (polycrystalline) silicon films. We quote from the 2001 Annual Report: "Thin-film silicon holds great promise as a semiconductor that can be produced economically on a large scale. Its exceptional properties for photovoltaic energy conversion have already been demonstrated and are the subject of intensive study worldwide. Yet the entire field of heterogeneous thin-film silicon (often referred to as polycrystalline silicon) is remarkably poorly understood. This is not too surprising, given our limited understanding of one of its constituents, amorphous silicon, in particular in its hydrogenated form. In the thin-film silicon, the interfaces between crystalline grains and between crystalline and amorphous regions appear to be of particular importance, since they are likely to lead to the exceptionally large optical absorption observed in these films, which exceeds that of both c-Si and a-Si:H. The understanding of the interfacial regions is, however, entirely lacking. What is their fractional volume, and how can it be controlled? Where is the hydrogen located in these films, and what is its role in their electronic properties? A better understanding of these fundamental questions is crucial for the development of better photovoltaic devices, and for any other technological application as well. This is the objective of the present study.

We will use the same elastic measuring technique used previously to study crystalline and amorphous films, utilizing the extensive experience and skills in film preparation and characterization available at NREL. Through such measurements, we hope to contribute to the understanding of heterogeneous solids in general, and to the development of better and more durable photovoltaic devices in particular. The thin films are deposited on a double-paddle oscillator etched out of high purity silicon. The bare paddle has an extremely small damping, and is therefore highly sensitive to any disorder in the film."

The research performed can be presented under three separate headings.

- (1) Properties of the bare oscillators
- (2) Damping in amorphous silicon films
- (3) Disorder in thin-film silicon

We will report our findings below under these three headings.

Report

- (1) Properties of the bare oscillators

The secret for the successful use of silicon oscillators for the study of the elastic properties (and thus, hopefully, of the hydrogen present in them) is that they have an

extraordinarily high mechanical quality, i.e. a very small internal friction. Thus, even nanometer-sized films can be detected.^{(1), (2)}

In the early work, only one of the normal modes had been used. However, on these oscillators, several normal modes had been seen, with frequencies ranging typically from 300 Hz to 12 kHz. The prospect of being able to use some, or even all of them for the thin film study over a wide range of frequencies led us to study the different modes in detail. This work has been reported.⁽³⁾ Below, we quote the abstract of this paper

“Six low-frequency eigenmodes of a double-paddle oscillator have been measured and have been identified with a finite-element model. The internal friction Q^{-1} of these modes has been measured in the range of 4–80 K. Only one of the oscillator’s modes has a $Q^{-1} < 3 \times 10^{-8}$ below 40 K, which is furthermore very reproducible. All other modes have a higher internal friction which is not as reproducible and also sometimes changes after thermal cycling. It is shown that the internal friction of the different modes is related to the restoring force needed to hold the oscillator in place. The finite-element model is used to predict the damping of the different modes.”

The major conclusion of this work was that only two modes, with fairly similar frequencies, showed the exceptionally small damping. This led us to explore the cause of the damping, in the hopes of finding ways of reducing it. In order to identify the place where the damping occurs, we mounted the sample holder in the cryostat with a heavy piece (~ 500 g) of BeCu in between. This alloy is known to have itself very little damping and was expected to reduce the transmission of elastic vibrations to the cryostat where they might be damped in many places (solder, plastically deformed metals, and so on). This had no effect on the damping, from which we concluded that the observed damping is not occurring in the cryostat itself. It was then suggested by our colleagues at the Naval Research Lab that, based on their finite element analysis, paddles on which the legs carry protrusions (“fingers”) with carefully determined spacings should transmit less energy into the sample mount. Fig. 1 shows two of our standard paddles, and one with fingers, all manufactured in Cornell’s Nanofabrication Facility. The results shown in Fig. 2 were disappointing. The damping was reduced, but only by less than a factor of 2. This observation strengthened the suspicion that the residual damping may indeed be intrinsic (thermo-elastic damping). This interpretation was studied by Photiadis and co-workers.⁽⁵⁾ Their conclusion was that while this damping mechanism could account, even quantitatively, for the damping above ~ 50 K, it should not work at all at lower temperatures.

The conclusion at this point is that the residual damping below 50 K is not understood. Thus, we see no way of reducing it further.

(2) Damping in Amorphous Silicon Films

A question of fundamental interest is whether the internal friction observed at low temperatures in amorphous silicon films can be blamed on the spins of unpaired electrons, reason being that in the perfect, fourfold coordinated amorphous silicon lattice no atomic tunneling is expected. This work was undertaken by Tom Metcalf, a graduate student working in our group. We quote from the paper he published⁽⁶⁾:

“The internal friction of e–beam silicon was measured in a magnetic field between 0 and 6 T, from 1.5–20 K, and was found to be independent of the field to better than 8%. It is concluded that the low energy excitations observed in this experiment are predominately atomic, not electronic, in nature.”

We have also extended our work on the effect of ion implantation in silicon to arsenic ions. The effect shown in Fig. 3 is qualitatively similar to what had previously been reported for boron and silicon ion implantation.⁽⁷⁾: A narrow relaxation peak at ~ 40 K, and a flat temperature–independent damping below 10 K. The peak is well described with a Debye relaxation expression:

$$Q^{-1} = \Delta \frac{\omega\tau}{1+\omega^2\tau^2} \quad (1)$$

$$\tau = \tau_0 e^{E_b/kT} \quad (2)$$

Through measurements at two different oscillator frequencies, 400 Hz and 5400 Hz, the activation energy E_b was determined to $E_b = 0.08$ eV. The peak is independent of the implanting species, and disappears during annealing at ~ 520 K. All these observations confirm our previous conclusion that this peak is connected with silicon divacancies. We also studied the divacancy concentrations as a function of dose, see Fig. 5. While the linear rise of divacancy concentration with dose is easy to understand, the saturation observed at high doses is not. In trying to understand the latter, we were lucky to interest one of the theorists in our laboratory, Professor Tomas Arias, to explore the coupling of divacancies to the lattice strains. He and his graduate student, Hande Ustunel, were able to determine the coupling strength from first principles. When they used this strength to determine the divacancy concentrations, however, they came up with concentrations two orders of magnitude smaller than the ones we had determined, based on the work cited in Ref. (7), and which are shown in Fig. 5. In spite of much effort, this discrepancy has not been resolved at this point. This has put our attempts of understanding the saturation of divacancies on hold, and with it the write–up of this work for publication. Currently, our colleagues at the NRL are also becoming interested in this issue, and it is hoped that his log–jam will be broken soon.

In another effort to understand the origin of atomic tunneling states in amorphous solids, we extended the investigation to amorphous germanium and carbon films, in which effects were observed similar to those in silicon. We quote here from the summary published on this work⁽⁸⁾:

“The density of low–energy excitations in tetrahedrally bonded amorphous thin films shows a wide variation, deviating from the universality established for all other amorphous solids without exceptions for over the past 30 years. Their magnitude, as determined by the temperature-independent internal–friction plateau below 10 K, is below the lower limit of the ‘glassy range’ (1.5×10^{-3} – 1.5×10^{-4}), in which all other amorphous solids have been found to lie. Film preparation methods, hydrogen content and annealing are all important parameters leading to the dramatic changes in the density of the TLS. We suggest that the peculiar properties of the low–energy excitations in

these amorphous thin films is related to the unique tetrahedral bonding of the atoms. The atomic motion, required for the tunneling states, may originate from the locally underconstrained regions and may therefore be sensitively dependent on the perfection of the CRN. It may be that the tunneling states are indeed caused by loosely bonded individual atoms or clusters of atoms as first suggested by Phillips (1972).”

(3) Disorder in Thin Film Silicon

This work, constituting the majority of our effort under support by this Grant has been reviewed⁽⁹⁾, and we quote here only the Abstract:

“We have measured the low temperature internal friction of nanocrystalline silicon films produced by HWCVD and by PECVD with different hydrogen dilutions of the silane gas. With decreasing volume fraction of the amorphous phase, the internal friction increases, contrary to our expectation. The results suggest a large disorder in the crystalline phase, comparable to that of amorphous silicon. The nature of this disorder is unknown.”

We can thus summarize this part of our research by saying that our measurements have shown a variety of elastic damping processes that are not understood at this time. Since the disorder observed here may also influence properties of importance for the practical applications of these films, it seems to be of more than academic interest to find ways to control this disorder. It is unfortunate, however, that there remain so many open questions, and no time to answer them!

List of publications resulting from this Grant

“Internal Friction of Amorphous Silicon in a Magnetic Field,” by T.H. Metcalf, Xiao Liu, and R.O. Pohl, Phys. Rev. B **61**, 9902 (2000).

“Normal Modes of a Si (100) Double-paddle Oscillator,” by C.L. Spiel, R.O. Pohl, and A.T. Zehnder, Rev. Sci. Instr. **72**, 1482 (2001).

“Low Temperature Internal Friction of Amorphous and Nanocrystalline Silicon,” by C.L. Spiel, Xiao Liu, B.P. Nelson, Qi Wang, R.S. Crandall, and R.O. Pohl, ECS Proceedings Volume 2001–10, p. 302 (2001).

“Disorder in Tetrahedrally Bonded Amorphous Solids,” by Xiao Liu, D.M. Photiadis, H.–D. Wu, D.B. Chrisey, R.O. Pohl, and R.S. Crandall, Phil. Mag. B **82**, 185 (2002).

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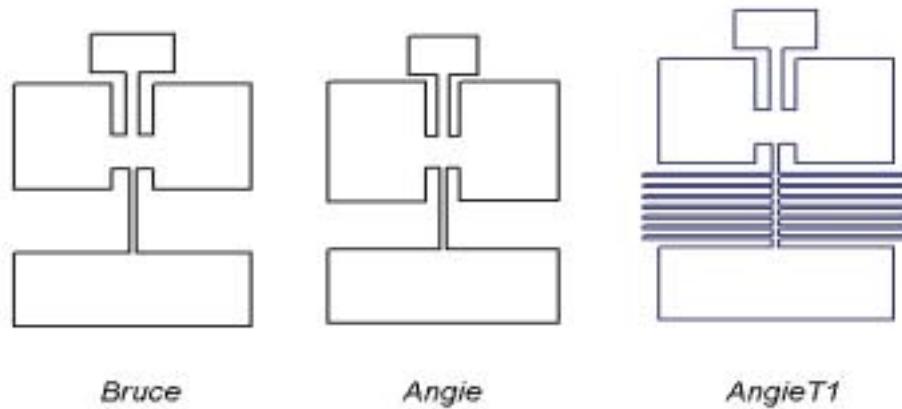


Figure 1: Design of three double paddle oscillators used in this investigation, consisting of a “head” and two “wings” which are connected by a “neck”. They are attached to a “foot” by “legs”, overall height ~ 3 cm. They are attached to the cryostat by means of epoxy, or by dry-clamping, to an Invar block, the thermal contraction of which matches that of silicon. The paddle designs have been called after their designers, Bruce White and Angie Sarkissian. Note the “fingers” on the leg of Angie T1, which were added in an attempt to reduce the damping.

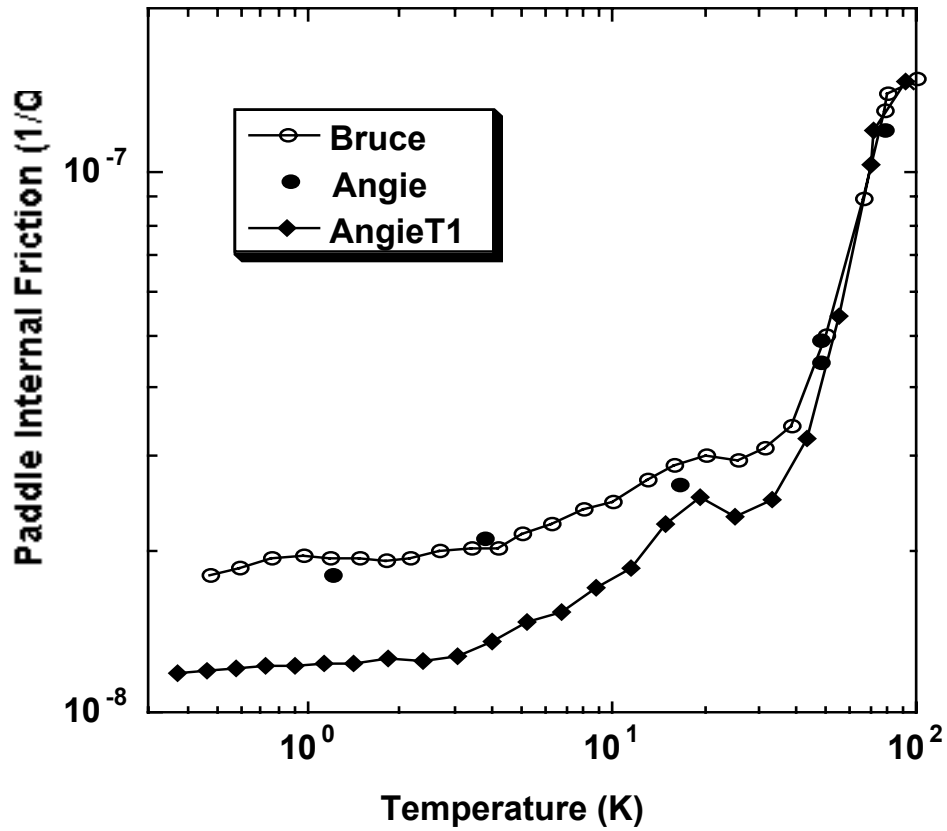


Figure 2: Internal friction of the three oscillators shown schematically in Figure 1. It varies only insignificantly for the three designs, leading to the suggestion that the damping may be intrinsic even at lowest temperatures [4].

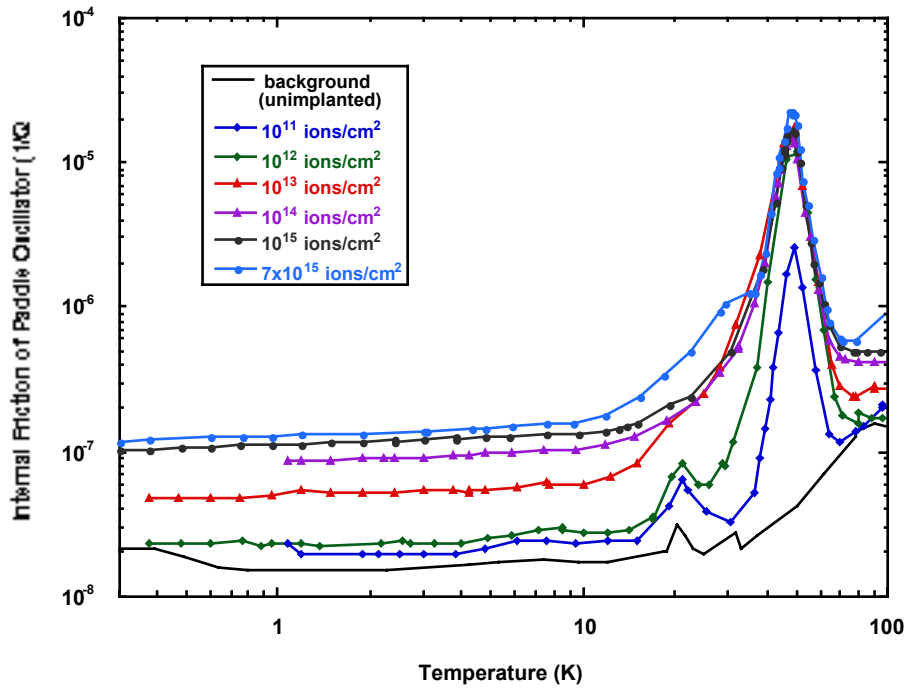


Figure 3: Internal friction Q_p^{-1} of a paddle oscillator with six consecutive arsenic implantation doses. Frequency: 5400 Hz.

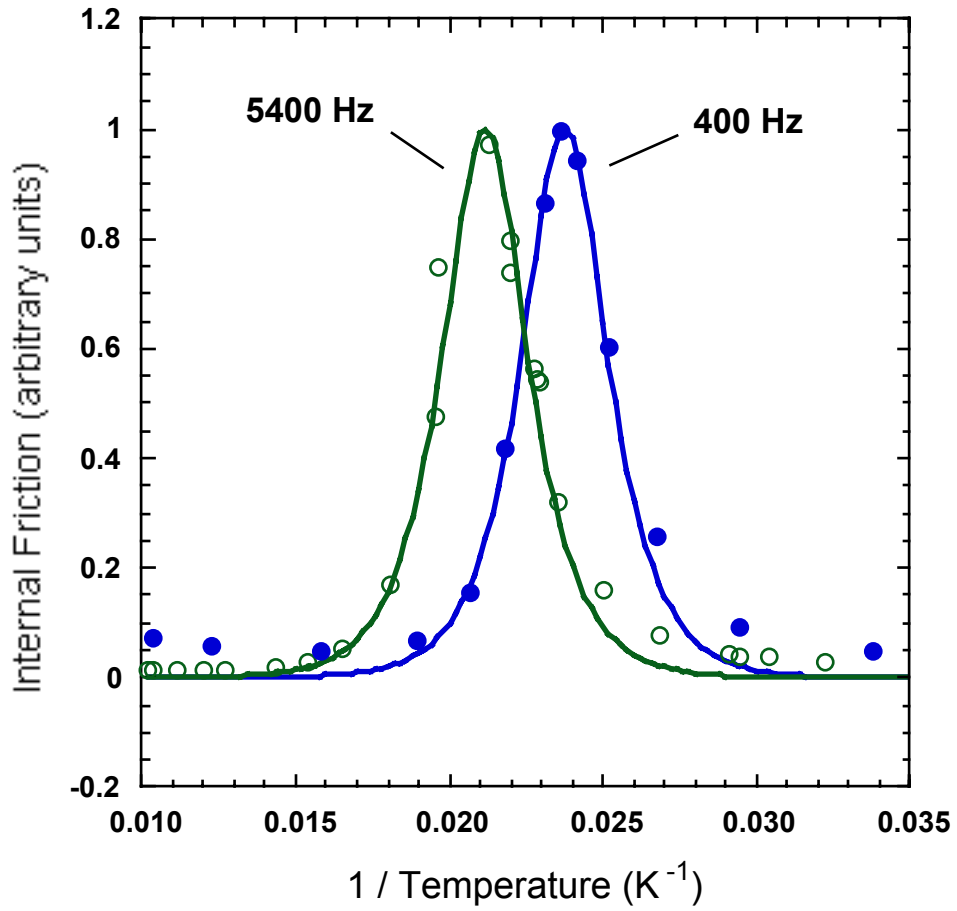


Figure 4: The 40 K peak in implanted silicon measured at two frequencies. Curves are Debye relaxation peaks (eq. (1)). From the shift with frequency, the activation energy E_b of 0.08 eV is determined.

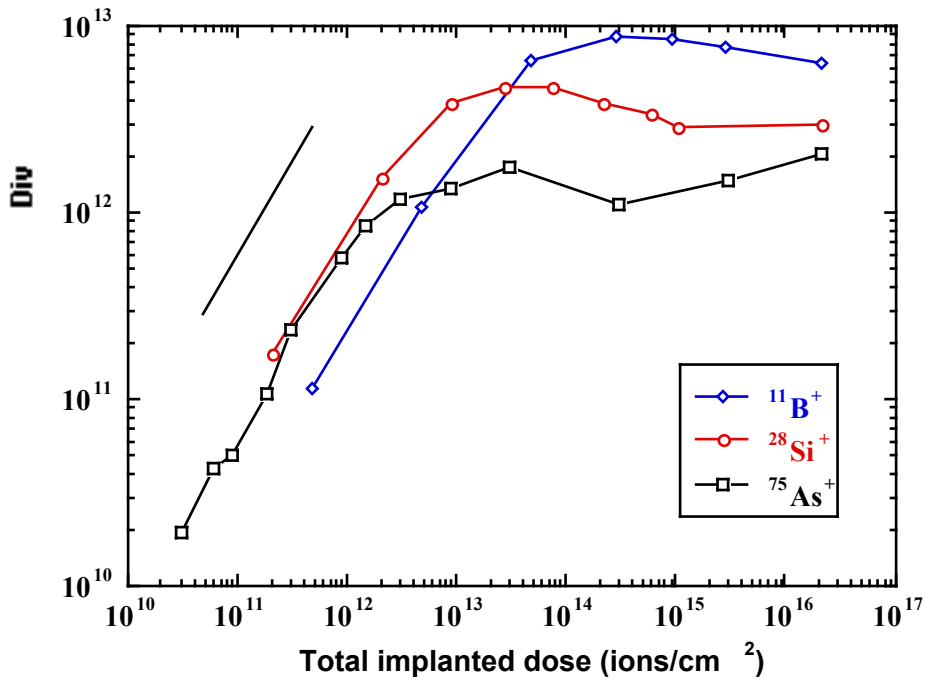


Figure 5: Two-dimensional divacancy concentration as a function of total implanted dose. Up to 10^{12} ions/cm² the concentrations vary in linear proportion with the arsenic dose (see the line in the upper left hand corner). Measurements at 5400 Hz.

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