Conductivity Transitions in Nanocrystalline Silicon Films as a Function of Oxidation

Jake Novotny

Submitted under guidance of Professor James Kakalios to the University of Minnesota Digital Conservancy in partial fulfillment of ending requirements for the Undergraduate Research Opportunities Program, University of Minnesota – Twin Cities.

September 18, 2016

Abstract

The electronic properties of nanocrystalline silicon (nc-Si) thin films were investigated, measuring the conductivity of a nc-Si film which had been stored under vacuum since its fabrication. Of particular interest was a transition in the electrical conduction mechanism caused by oxidation: an effect previously observed in Kakalios labs.[1] Conductivity was measured as the temperature was varied in the range 305K – 470K after varying periods of atmospheric exposure. Assuming the conductivity form $\sigma(T) = \sigma_o \exp[-(T_o/T)^{\kappa}]$, the Zabrodski analysis of the film in ramping down annealed states before atmospheric exposure gave a best fit of $\kappa \sim 0$, corresponding to a power law of temperature, $\sigma(T) \sim T^n$ with $n \sim 23$. After ~ 100 ksec of atmospheric exposure, the same analysis suggested $\kappa \sim 1.0 - 1.6$, signaling a transition in the conductivity dependence on temperature; however, these κ did not converge to a common value as expected. Additionally, in ramping up from annealed states, the Zabrodski analysis took on a completely different curvature, displaying a sawtooth character in measurements before the conductivity transition. The apparent inconsistencies in expected results show further experiment is necessary to fully classify nc-Si films.

Introduction

There is considerable interest in large scale coating thin films for many applications, such as solar panels and flat panel displays. Hydrogenated amorphous silicon (a-Si:H) provides an inexpensive way to cover large areas with conductive material but suffers from significant photovoltaic degradation through the Staebler-Wronski effect. It has been

reported, however, that placing nanocrystalline inclusions in a-Si:H films may reduce these deficiencies. An extension of this work is recent theoretical and experimental investigations of the properties of free-standing nanocrystalline silicon (nc-Si) thin films.[2] The films of interest consist of silicon nanocrystals coated in an amorphous shell. Such films are made by depositing silicon nanocrystals over metal electrodes on a glass substrate in a Plasma Enhanced Chemical Vapor Deposition chamber; the same process is used to make amorphous silicon films, with the nc-Si films also being spread in thin layers.[3]

Beyond the Staebler-Wronski effect, there is significant interest in the effect of atmosphere exposure on nc-Si films. In a previous work by Brendon Jones of Kakalios Labs, an apparent transition in the mechanism of electrical transport was observed in a nc-Si film after sufficient atmospheric exposure.[1] While potential changes due to light exposure were reversible by annealing the sample, this transition, caused by oxidation, was not.[1] The films have little theoretical framework, but it is expected they would resemble semiconductors, with a conductivity dependence given by

$$\sigma(T) = \sigma_o \exp[-(E_a/k_B T)] \quad (1)$$

where E_a is the activation energy of the film, T is the temperature, and k_B is Boltzmann's constant. In a previous work by Bodurtha and Kakalios, it was found the anomalous hopping expression

$$\sigma(T) = \sigma_o \exp[-(T_o/T)^{\kappa}] \quad (2)$$

with $\kappa \sim 3/4$ may be more appropriate for a-Si:H films with nc-Si inclusions.[3] Such a functional behavior can be investigated using the Zabrodski analysis, where the quantity

$W = d\ln\sigma/d\ln T$ is called the reduced activation energy and is plotted against temperature on a log-log scale. A functional form as in eq. (2) would then yield a straight line with a slope of $-\kappa$.[4] The anomalous hopping expression, (2) was investigated by Jones, where it was determined a freshly deposited nc-Si film had $\kappa \sim 0$, potentially corresponding to a power law conductivity dependence on temperature, $\sigma \sim T^n$ with $n = W$.[1] After being exposed to atmosphere for ~ 1000 ks, the conductivity reverted to the form given by eq. (2) with $\kappa \sim 0.7$.[1] However, the transition itself was not documented, as the original goal of Jones's work was to analyze the effects of long term atmospheric exposure, while the transition in conduction mechanisms occurred on much shorter time scales. Additionally, Jones's work investigated only a single state (that is, the annealed state when measured upon cooling from a high temperature anneal) of the sample. This project aimed to build on Jones's work by measuring a new sample, similar except for a slight geometrical factor. The goal was to document the transport mechanism transition as well as further classify the properties of nc-Si thin films for future investigation.

Conductivity Measurements

A potential difference of +50 V is applied across the sample's co-planar electrodes, and the resulting current is measured. The sample sits inside a vacuum chamber (pressure less than 5 mTorr), mounted on a copper block containing a resistive cartridge for temperature control from 305K to 470K, where silver paint was used to keep the sample in solid thermal contact with the block. Two wires were attached to the open ends of the electrodes, using silver paint to secure a consistent electrical connection. A specially

designed small glass window at the top of the chamber allowed the sample to be lightsoaked with a 75 W tungsten bulb, but remained covered otherwise.

The condition of the film was classified into three distinct states; State O represented the sample with residual effects from the atmospheric exposure, only present just after being brought to vacuum conditions. State A was the annealed state of the sample (470K for at least two hours), considered to be the pure, unadulterated state of a nc-Si film under vacuum conditions after any water vapor adhering to the film is removed by annealing. Finally, State B was the lightsoaked state of the film following illumination with the W-Ha lamp for at least three hours. Conductivity measurements were taken while ramping the temperature at a steady rate of 1 K/min in the range 305K to 470K. For each atmosphere exposure time, the sample was brought under vacuum, and the conductivity was measured as follows: first ramping up from a start temperature of 305K to 470K, the State O conductivity measurement. Next the sample annealed at 470K for 2 hours, entering the first annealed state, State A1. After this, conductivity was measured ramping down, then up, then down again, and these individual states were labeled with the postscript d1, u, d2 respectively. At this conclusion, the sample was lightsoaked at 305K for $\sim$ 3 hours. The conductivity was then remeasured while increasing the temperature, the State B measurement. Finally, the sample annealed again at 470K for 2 hours, entering State A2, where the states A2d1, A2u, A2d2 were recorded, completely analogous to the State A1 conductivity measurements. The conductivity ramping ("condramping") is depicted schematically in Figure 1.

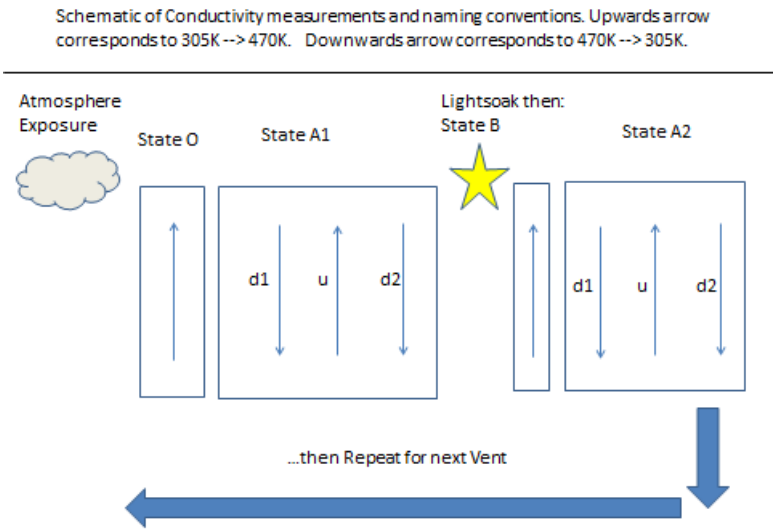

Figure 1: a schematic outline of conductivity measurements and naming conventions. The sample is exposed to atmosphere, or "vented," then brought to vacuum and cycled through a series of measurements before being vented again. State A1d1 was the state used in Jones's analysis.[1]

In addition to condramping, IV plots were taken at 305K before the State 0 condramp, before the first anneal, and after the final condramp, A2d2. These were used primarily to ensure the electrical connections remained intact (linear I-V characteristics are expected) and for future reference when comparing new films with possibly differing geometry factors.

Results

The conductivity temperature dependence for State A1d1 (the state documented in Jones's work) was found to transition from $\kappa \sim 0$ to $\kappa \sim 1$ over a cumulative atmospheric

exposure time of ~ 100 ks. Interestingly, the κ values for all other ramping down annealed states differed from that of A1d1, as shown in Figure 2.

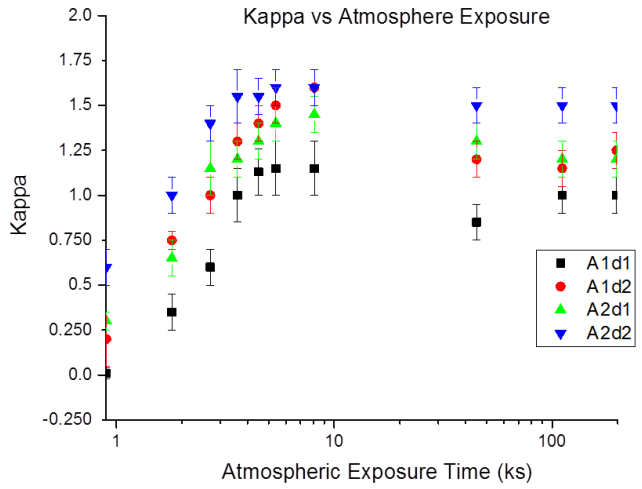

Figure 2: Kappa values from the Zabrodski analysis of the ramp down annealed states of the sample plotted against a logarithmic time scale. Note the markedly different kappa values across the states, yet the states A1d1, A1d2 and A2d1 A2d2 respectively are theoretically identical. The discrepancy appears to be consistent, rather than random.

Even more interesting, however, was an apparently different conductivity temperature dependence when ramping the temperature up from 305K to 470K. While ramping down, Zabrodski analysis suggested each state could be fit to a line with slope starting at 0 and becoming increasingly negative, as shown in Figure 3. But while ramping up, the Zabrodski plot had a clear divergence from a linear fit. Instead the conductivity transition was characterized by a "sawtooth" behavior initially, flattening to a line of slope 0 with longer exposure time (see Figure 4). This sawtooth behavior could attributed to two

distinct activation energies, but the origin and meaning of multiple activation energies is not well understood.

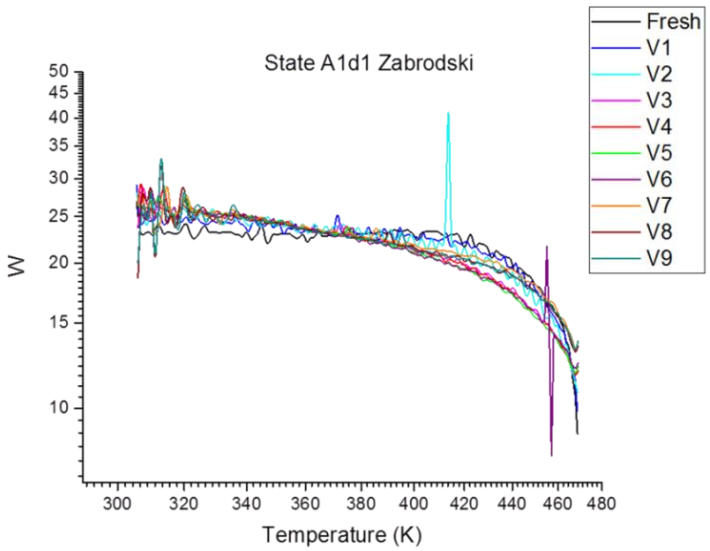

Figure 3: Zabrodski analysis of State A1d1 for various atmosphere exposure times. "Fresh" corresponds to the state of the sample after being put under vacuum in as little time as possible after its fabrication, and "VX" corresponds to the X^{th} atmosphere exposure. The times of atmosphere exposure varied between measurements, for detail see Figure 2. Zabrodski analysis suggests an initial slope of ~ 0 in the fresh State A1d1 transitioning to a slope of ~ -1, corresponding to $\kappa \sim 0$ and $\kappa \sim 1$ respectively.

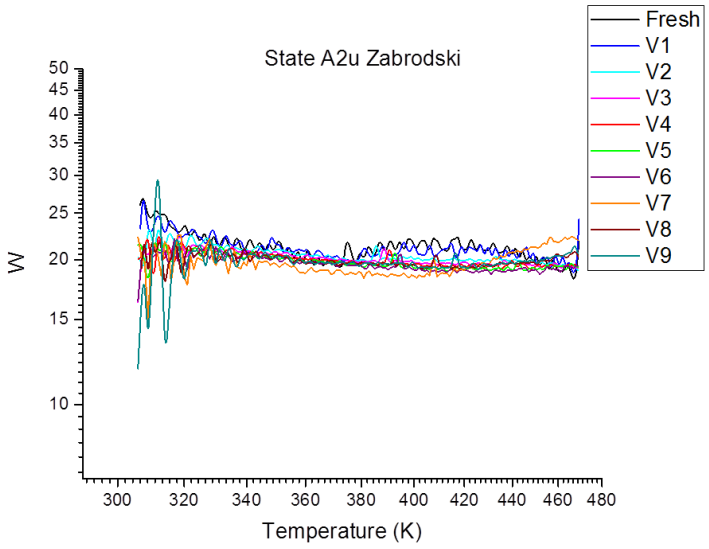

Figure 4: Zabrodski analysis of State A2u for various atmosphere exposure times. "Fresh" corresponds to the state of the sample after being put under vacuum in as little time as possible after its fabrication, and "VX" corresponds to the X^{th} atmosphere exposure. The times of atmosphere exposure varied between measurements, for detail see Figure 2. Note the sawtooth character initially present in the sample at fresh flatlines around V2.

Zabrodski analysis of State B plots mimicked the behavior of the other ramping up plots from the annealed state A without any significant change in magnitude of the conductivity, while State O Zabrodski analysis was sporadic; the conductivity observed in vacuum conditions was corrupted by leftover atmospheric effects before being annealed.

Another striking feature of the Zabrodski analysis of ramping down annealed states was a "nosedive" curvature present at temperatures above ~ 450K, as in Figure 3. While this was more pronounced in the d2 measurements, it was present in all ramping down

Zabrodski plots. This curious behavior was also noticeable in conductivity plots, shown in Figure 5. The curvature present in the high temperature data suggests changes in the activation energy of the sample.

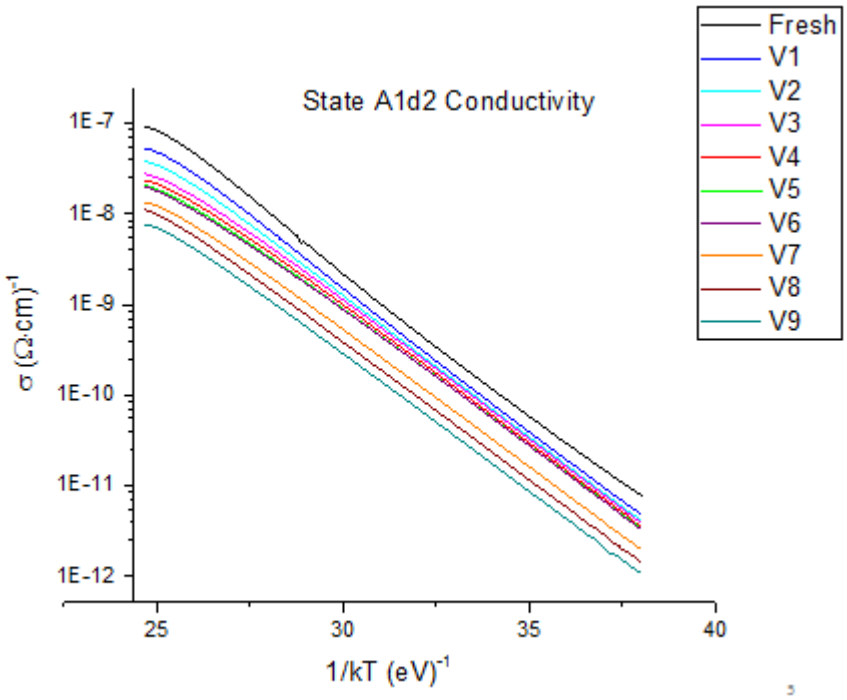

Figure 5: Conductivity plotted against 1/kT on a Ln-Lin scale for various atmosphere exposure times. According to (1), the slopes represent the activation energy of the sample. Note the curvature present in the high temperature region, corresponding to changes in the sample's activation energy.

Conclusions

The conductivity transition caused by oxidization was documented and found to be analogous to the sample in Jones's work, but the full results of the Zabrodski analysis leave many unanswered questions.[1] While the transition was characterized by a change in κ from 0 to ~ 1.0-1.6 when ramping down, it was characterized by an initially present sawtooth behavior flattening to a straight line when ramping up. In all cases where κ ~ 0, both

ramping up and down, the potential power law of temperature correspondence, $\sigma \sim T^n$ yielded n ~ 21-24. Further study of these films is necessary in order to determine if such a the conductivity does indeed follow this power-law expression.

The differing κ values were not investigated in Jones's original work, as he was only interested in State A1d1. The observation of changing κ value reported here is interesting for many reasons. Foremost, the states A1d1, A1d2 and A2d1, A2d2 should be exactly identical, yet while the overall change of the κ values with oxidation time is similar, there is a significant quantitative difference in κ for these different measurement runs . While the discrepancy could be due to measurement sensitivity, it seems unlikely given the κ values for the A1d2, A2d2 states were consistently larger than those of A1d1, A2d1. That is, Zabrodski analysis suggests that the conductivity measurements of a given state after a set atmospheric exposure were reproducible, but different states gave different behaviors. This surprising finding seems to suggest there is a unique feature of each state, even those which should in principle be identical, or there is an unseen bias in the analysis. Second and perhaps more importantly, the anomalous hopping expression (2) predicts $\kappa < 1$, yet other than State A1d1, the κ values were consistently greater than 1 at the final atmosphere exposure, a result which challenges our understanding of charge transport in these materials.

The other seemingly strange result was the rapid decrease in the reduced activation energy, W, at higher temperatures in the Zabrodski analysis of ramping down annealed states, which was observed, but not as prominently in Jones's work.[1] The radical shift from

a linear behavior suggests the expression in equation (2) is not appropriate in the high temperature range, but it could also indicate a state transition in the film; Figure 5 suggests the sample's activation energy beginning to change at high temperatures. Further investigation at higher temperature is required to draw conclusions of the validity of the form (2) and the meaning of the curvatures in Figures 3 and 5.

Acknowledgements

I would like to thank my faculty mentor, Professor Jim Kakalios for his consistent guidance and support for the duration of this project, as well as PhD candidate Zvie Razieli for showing me how to use the lab equipment and for making the samples described in this report. Their technical assistance and experience allowed this project to proceed efficiently and smoothly.

References

[1] Brendon Jones, *Conductivity in Nanocrystalline Silicon Films*, University of Minnesota Twin-Cities Honors Program, Kakalios Labs, private document.

[2] R. N. Pereira, D. J. Rowe, R. J. Anthony and U. Kortshagen, *Phys. Rev. B* **83**, 155327 (2011); Ting Chen, K. V. Reich, Nicolaas J. Kramer, Han Fu, Uwe R. Kortshagen and B. I. Shklovskii, *Nature Materials* **15**, 299 (2016).

[3] K. Bodurtha and J. Kakalios, *J. Appl. Phys.* **118**, 215103 (2015).

[4] A. G. Zabrodskii and I. S. Shlimak, *Sov. Phys. Semicond.* **9**, 391 (1975).