Photo Voltaic Silicon: Casting Heat Transfer
Induced Stress and Defects

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0.1 Introduction to the Growth of Silicon

Silicon can either be examined with eddy current induction techniques while it is solidifying and cooling or afterwards when it is cold and possibly sectioned. Silicon is a complex thermal material having three uncommon features. First its melt is metallic and high density going to a lower density solid. Second, it has a transition from opaque to transparent in the infrared, while it is still warm enough to allow internal radiative heat transfer to dominate thermal conduction while the solid will easily deform plastically. Third, with rapid growth there is a high concentration of retained self interstitial defects from the solidification process. It is easier to extract information during the cooling process rather than after cooling is complete. This is because transient events will be monitored and their relationship to the final product can only be evaluated if they are detected. It is difficult to unravel deformation that could have occurred at three different times by just looking at the residual stress in the final product. The second reason for wanting to study the dynamics at the time of production, is that current modeling practice has not integrated accurate grey body heat transfer calculations, with the optical refraction and reflection. The optical activity can concentrate internally reflected radiation. The temperature and frequency dependent internal emissivity and absorption coefficients are not known for silicon and are difficult to determine. Silicon’s high refractive index which increases with temperature, makes it extremely difficult for radiation to strike the surfaces close to the normal and escape. Most of the radiation is reflect back inside to be reabsorbed in the hot core of the ingot. This activity dominates the heat transfer in temperature regimes where plastic yielding can occur. An accurate understanding of this phenomena gives the engineer a way to design ingot geometries and set the furnace cooling profiles to minimize deformation and allows one to design an optimum melting and cooling system.
0.1.1 Grown in Point Defects

The growth of single crystal silicon from a melt can occur quite rapidly, in excess of 1 mm/minute which is near 30,000 layers of silicon per second being laid down. This high speed deposition is only allowed by the fact that the liquid state is metal and supports no long range structures that if incorporated in the lattice would disturb the crystallinity. The melt’s density decreases going to the solid. If a local high density region in the melt has a life time of greater than 30 microsecond, it could easily be trapped in the solidification and yield a self interstitial in the final solid. The high concentration of self interstitial in silicon are probably trapped by this dynamic process which is much greater than the calculated equilibrium concentration. These self interstitial defects and vacancies will contribute to silicon’s high temperature ductility through point defect driven primary creep and inhibit or delay dislocation creep to relax the thermal stresses. Thus slowly grown silicon would be expected to start dislocation creep a high temperatures earlier because point defect creep would be suppressed.

Diffusion of point defects at high temperatures just below the melting point will occur in an environment of low internal stresses. These two populations of vacancies and interstitial silicon will tend to annihilate. As the system cools establishing a cool shell and a hot core either in CZ or bulk cast growth, there will be the onset of primary creep to relieve these stresses. This primary creep will be based on point defect migration. Vacancies will migrate to regions of high compressive stress and self interstitial and foreign interstitial defects will migrate to regions of elevated tensile stress. This point defect migration results in the well known point defect minimum band found in CZ silicon growth with a vacancy rich core.

0.2 Optical Properties of Hot Silicon

The black body peak between 900°C and 1200°C falls in the infrared band with wavelengths between 1 and 2 microns(1). As the intrinsic conductivity of silicon falls with a reduction of temperature the optical absorption coefficient is also decreasing and the mean penetration depth of the radiation increases. The number of electrons in the valance band depend on an exponential term $e^{-\frac{Eg}{kT}}$ which is temperature sensitive as shown in figure 1. When the optical penetration depth is on the order of a few millimeters large changes in thermal conduction occurs as there are two competing processes at work in moving energy, conduction and radiation. The problem is that the radiation can move the heat efficiently in a direction opposite to the cooling gradient because of reflection and refraction. Graphically these processes are shown in figure 3.

Within the transition region, radiation will be absorbed and emitted continually. The equation describing the emission on any plane within the solid(3) is of a black body emitter into a media with a dielectric constant, n.
In equation 1 the $\sigma$ is Stefan-Boltzmann constant, the refractive index, $n$, and the temperature. For materials with large refractive indexes the internal radiation fluxes will be large. In the case of silicon at room temperature $n \approx 3.45$. With increasing with temperature the refractive index rises. This increases the black body internal radiation load by more than a factor of 10 compared to something close with a refractive index close to 1. So internal radiation heat transfer is enhanced and competes against standard thermal conduction which is suppressed at elevated temperatures.

The principle parameter controlling physical optics within the crystal other than absorption is the dielectric constant and its property of increasing with temperature will force any ray approaching a cooler outer surface from inside to bend away from the surface. If the angle of incidence from the normal is greater than 6° of arc the ray will be completely internally reflected(11). A reflected or refracted ray will find its way back to hot core or possible be focused to a hot spot such as an optical caustic.

### 0.3 Stress in Cooling Silicon

In cast cubes of silicon, corner and edge reflection and refraction may maintain locally steep thermal gradients through the transparency transition and drive local yielding because of local thermal expansion and shear stresses developed at the corners and edges.
Figure 2: Comparison of the internal radiative heat flux in silicon verse conductive heat fluxes for 4 different gradients from 100C/cm to 10C/cm

Figure 3: The hot core slow cooling while the outside regions become transparent. 900 C set up strong compression stresses in the center and tension in the shell. Once plastic deformation begins on the weakest face, the symmetry of the deformation will tend to 2 fold. When the ingot is finally at cool and uniform in temperature, the states of stress will have changed sign.
The weakest face on the shell is the warmest face. In the case of the cast cube this would be the top face while ignoring the corners and edges yielding would be expect to start on top and propagate around the cube. However, with the corners and edges producing stress concentration over what would be found on a flat face the yielding would be expected to occur in those regions with the highest stress gradients. The outer surfaces will see a tensile stress as they cool making plastic deformation easier than if the surface were in compression.

0.3.1 Gradients in Thermal Contraction of Silicon

Thermal gradients of the cooling system will drive yielding. If Silicon is opaque above 1200°C, the heat transfer problem is one of simple thermal conductance with near linear and monotonic thermal gradient to the surface. Because of the corner and edge shape these conductance gradients may drive dislocation creep at high temperatures. With the crystal sitting in a transparent crucible these gradients should be minimized except if there is local bonding of the crucible to the silicon. However, once the outer regions of the crystal begin to go into the grey body region where it is semi transparent, the optical dynamics of silicon take over the bulk of the heat transfer. Radiation into the silica is inhibited relative to the bulk because of the low refractive index of the silica crucible. The temperature dependence of the refractive index insures that any light that is not propagating normal to the surface within the silicon is bent away from the surface and is internally reflected into the cavity between the wall and the hot opaque core. Conductive heat transfer is also taking place but with low gradient near the surface. This leads to a much higher gradient at the transition to the opaque boundary and more defined tensile shell stress. A good example of thermal gradients within CZ silicon is shown in figure 4.

The reason the grey body is very efficient at dumping optical radiation into the cavity and reabsorbing the radiation is the high dielectric constant of silicon. One can get a picture of this if one places an imaginary source plane in the transition region and estimates the black body radiation coming off of this plane. The amount is proportional to temperature at the 4 power and the square of the dielectric constant.

The square of the dielectric constant assures one that the radiation dumped into the cavity is at a rate of one order of magnitude higher than that of a normal black body. The relative radiative heat transfer to the conductive heat transfer as a function of temperature is shown in figure 2.

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( The result is a thermal gradient realized by the combination of the enhanced pumping of internal radiation, the highly reflective wall and the optical effect of limiting radiation from ever reaching the wall. ) In order, to demonstrate this effect we took a 2” diameter 12” long rod of silicon and placed the 4” ends into two furnaces one at 400°C and the other at 900°C. The outside of the rod was sheathed in .5” thick micro alumina zicar tube. An encircling coil scanned the rod and produced the fir tree like chevrons for isotherms pushing a hot core down the center of the rod as shown in figure 6.
Figure 4: 4 inch dia CZ silicon during growth showing isotherms and hot core.

Fig. 6.6.3. The radial temperature distribution in crystal no. 36 estimated from fig. 6.6.1. ○ are obtained directly from fig. 6.6.1. ● are extrapolation. The first isotherm (1410 °C) is at z = 0. The isotherms are spaced every 30 °C.
Figure 5: Refraction of radiation towards the higher temperature regions driven by the increasing value of the dielectric constant with temperature
Unless all these optical effects are included in a global radiative and conductive heat transfer model there is little hope of making even an estimate of the internal gradients. An additional problem with the calculation is the need of the frequency dependent emissivity and absorption coefficients to do the optical calculation as a function of temperature along with the dielectric constants properties at these elevated temperatures. It is easier to measure these gradients in an intrinsic semiconductor such as silicon using an eddy current technique than to model specific cases. A model just using thermal conduction for silicon as compared to the measured thermal gradients is shown in figure 7.

There is one more feature that is characteristic of a cooling silicon ingot as it drops into the transparent region and that is something that can be referred to as a cooling catastrophe. If the ingot has an exposed to cool face then the cooling becomes very rapid at a particular temperature. This is inhibited in CZ silicon by putting on a long taper at the end and using radiation reflecting shields higher in the growth chamber to allow the crystal to cool slowly. In figure 8 a 4" crystal was grown to about 12" length and then raised slightly above the melt. The crystal was monitored in time by scanning the encircling probe. The cooling catastrophe can be seen to occur at different levels up the crystal in time as it cools. This is actually a measure of a very sharp axial gradient that forms in the transparent region by the strong internal radiative processes.

0.3.2 Creep, Yielding and Slip Bands

The stresses that drive the initial deformation of the cooling ingot have a tensile character on the outside and compressive stress on the inside. The outside shell yields via two processes, primary creep where a vacancy flux moves to the core and the interstitial flux moves to the outside wall, leaving the classic demuded zone at the point where the stress changes sign. The second process is dislocation
Figure 7: Comparison of experimentally measured isotherms with a thermal conduction only heat transfer model for CZ silicon (11ec)
Fig. 6.5.5. Cooling of four different crystal segments are followed in time. The crystal was lifted 25 mm above the melt surface before the power was turned off. The sensor positions were 50, 76, 101 and 127 mm above the melt surface.

Figure 8: Thermal catastrophe at loss of local hot opaque core (23ec)
creep which in silicon slip bands form. Below 1200°C when the material enters the grey body area on the walls, the thermal gradients can steepen creating higher stresses.

This is a critical time for massive dislocation yielding in silicon. During rapid CZ growth we have monitored this radial stress in situ in a number of runs, not realizing what was causing the two fold symmetry of the response around the ingot. However, as the system cools below 700°C the stresses reverse because as the core shrinks. This shrinking core has to work against the stretched shell to which it is bonded. This throws the shell into a state of compression and drives the slip bands into the core. This causes the core to yield because it is now in a tensile state.

Symmetry of yielding is important because it is a way to detect a residual stresses presence in an ingot. In a round ingot with no corners such as a CZ grown ingots, the yielding will start at one point on the periphery and radiate from that point as the rate of local work hardening pushes up the stress required to keep the initial slip bands active. That point would be the weakest point on the periphery, therefore, the warmest point. Thermal stress induced yielding is not a cylindrically symmetric process rather it lowers the symmetry to a two fold symmetry as the degree of deformation spreads around the periphery. In a cuboidal solid the presence of corners and edges along with the possible formation of optical caustic focusing patterns in the corners and edge regions forming hot spots so that local yielding should be expected in these areas.

0.4 Basic Multi Frequency Eddy Current Measurements

In the applications the designs of the high temperature sensor vary from single loops made of high temperature alloys to cooled loops depending on what properties and accuracies are required in the particular measurement. The sensor required for PV silicon cubes is a single absolute coil surrounding the box requiring a compensated coil system made of an alloy wire and 4 bore alumina thermocouple tube. This coil design requires a 4 wire vacuum connection port. Also, a thermocouple port would be useful to measure the temperature at one point on the coil. The coil design used was developed for high temperature applications where there are significant excursions in temperature and the coil material has a significant resistance coefficient as a function of temperature.

The room temperature sensors are usually multi turn probe coils used to scan structures. The optimum number of frequencies for simultaneous multi frequency inspection is three. So that the system maintains a high signal to noise ratio. If inverse analysis is used, the maximum in target information can be extracted with three frequencies.

There are two analysis techniques, one is to solve the EM boundary value problem with a range of material parameters, conductivity and dimensions and then fit the data to this set (1). The second technique is referred to as an inverse
analysis to relax a trial guess to the three frequency response function(18).
This can be done in two ways, one gives the liftoff of the probe and the mean conductivity of the sampled volume. The second technique assumes you know the coil liftoff and then you determine the conductivity gradient within the material. This is particularly useful for determining thermal gradients in silicon. Calibration is a key to all of the measurements and that is possible because in the operating system one can solve the exact boundary value problem for field reflection in six different geometries with a closed form solution. The field solving software is part of the Process Monitor IV operating system. The exact response integral can be determined for a know specimen. Calibrating on a know specimen allows all future measurement to be mapped into the measurement space to be analyzed in any of the modes presented above.

Measuring high temperature silicon in a resistance furnace, a narrow 1 hertz band width post detection filter is useful to minimize noise from the heating power network. Also, a calibration and multiplexer unit is necessary so that the individual sensor elements can be monitored so that a calibration can be effected. Even though there is only one active measuring loop in the system there are three other compensation elements in the circuit that have to be controlled.

The key feature of the Process Monitor IV measuring hardware is a very low noise and noise immune three channel calibrated quadrature detection system, coupled with closed form analysis software that can function for six different coil geometries to calculate the eddy current response to multilayered boundary value problems. In addition, there is inverse analysis software to reduce the data directly without having to use tables to extract volumetric conductivity changes and spatial geometry changes.

A complete list of reference to our published past work is given at the end of the paper. This represents only a fraction of the work done, because in most cases manufactures used our techniques to improve or control their processes, and do not allow publication.

0.4.1 Piezoresitivity in Silicon

( The detection of stress with eddy current measurement by us was an accident early in 2007 when examining very large CZ ingots that have yielded and of which X-ray maps of the slip systems were made. ) These silicon disks were transverse cut sections which were boron doped and high conductivity $> 10^3 \text{mhos/m}$ used for parts of ion etching systems. When a 3mm probe was placed normal to the flat surface 2cm in from the outside edge, the section was rotated so that a 360° scan of the conductivity could be made. All yielded specimens showed a 2 fold symmetry, one high point and one low point connected by a smooth curve. In material that was saw cut the response was smooth and much like a sine function. In the etched material there was a great deal of structure in regions that crossed the known slip band positions. The maximum conductivity variation was 5% in both the saw cut and the etched material. The dips in conductivity adjacent to some slip bands were of this magnitude.

The principle of why conductivity and stress are coupled in a semiconductor
is very simple and schematically shown in figure 9. There are three recent references (1,2,3) included below. The care that must be taken when using conductivity techniques is that one should know the dopant distribution which in CZ growth are flat on any section.

Also, the measurement should be accurate .1% and this required the use of a three frequency Process Monitor with the inverse software to remove and probe motion effects either due to the mechanics or the surface height variations. Small probe surface displacement variations swamp single frequency measurement attempts at this high resolution.

For the measurement of high resistivity PV silicon, the frequencies required are in the range of 100 MHz to 1000 MHz to get an accurate response. Calculations for the eddy current responses were done and are shown in Table 1. This requires a high frequency instrument including the inverse analysis software to make the measurement. It is expected that the scanning of cut and native surfaces will be much like what was found in the more highly doped silicon we ran our first trials on. We will do this trial with Process Monitor V shortly.

1: Calculated Responses to 4cm diameter probe 1mm liftoff, Nominal Conductivity of 1 ohm-cm is $10^2$ mhos/m †

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0.5 Acknowledgements

This is review of work done over a period of time starting with an IBM-Mitsubishi supported study of the heat transfer in CZ silicon. Also I want to thank Dave Witter of Anaxtal Corp for the samples containing the slip band structures. The information on the cast ingot silicon for poly crystalline solar cell production came from analysis of samples supplied by a variety of manufactures whose engineers were curious about dislocation damage but rather uninterested in the casting heat transfer.
Figure 9: Donor band gap is determined by the axial lattice parameter, which is dependent on the residual stress and its orientations.
Figure 10: 360° scan of the periphery of a 15” dia CZ ingot, that was cut and etched, showing the conductivity variation having a two fold symmetry. The local variation are associated with intense slip bands.

Figure 11: Sketch of scanning table for residual stress measurement by eddy current. Table should support at least 1000 kg with rotary table, either manual or driven. The vertical probe drive is 1 meter. This geometry allows tranverse, vertical or face mapping scans.
0.6 Appendix 1 Heat Transfer Functions

Total Radiant intensity and Hemispherical total emissive power of a black body (4) into a medium with index of refraction, n, from Stefan-Boltzmann law:

\[ e_b = n^2 \sigma T^4 \]

n is the refractive index, T is temperature in degrees kelvin and \( \sigma \) is the Stefan-Boltzmann constant, calculated \( 5.6696 \cdot 10^{-8} \frac{W}{m^2 K^4} \), experimental \( 5.729 \cdot 10^{-8} \frac{W}{m^2 K^4} \).

Thermal heat conduction equation:

\[ e_c = C(T) \frac{dT}{dx} \]

and \( C(T) \) for silicon from 300K to 1400K is:

\[ C(T) = .2934 + 2.4687 \cdot 10^4 T^{-1} + 8.4427 \cdot 10^6 T^{-2} - 5.567 \cdot 10^8 T^{-3} \]

0.7 Appendix 2 EM analysis of silicon response

Two cases are considered the first is an external coil surrounding the graphite box and crucible containing silicon and the second the graphite box has been converted to a monuturn so it does not participate in the reflection. The boundary value problem is solved for 5 frequencies 10,30,100,300 and 1000 hertz with a coil 1.04 meters in diameter and the graphite is 1.00 meter in diameter with a 20mm wall and the melt is .94 meters in diameter. The eddy current response is a vector reference to the applied signal which has magnitude 1 and a phase of 0 degrees. The reflected signal in conductors is always less than one with the phase delayed with respect to the applied field so it is a negative number between -90 and -180 degrees. The geometry use here is for a long solenoid which produces results similar to a single loop but computes much more rapidly and gives a measure of the signal expected from different conditions of the silicon charge.

APPENDIX 2, Table 1: Calculated Responses between Melt and Solid Silicon at 1440C with Graphite Box

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APPENDIX 2, Table 2: Calculated Responses between Melt and Solid Silicon at 1440°C with no Graphite Box, electrically eliminated with incomplete loop

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0.8 References


Eddy Current Background References by John Wallace:


18ec) "Gauging of Hot Tube and Bar by Multifrequency Eddy Currents" with C. Ihegwara, Sensors and Modeling In Materials Processing: Techniques


Phd Thesis on Eddy Currents Supervised

