

REASONS TO BELIEVE PULSED LASER ANNEALING OF Si DOES NOT INVOLVE SIMPLE THERMAL MELTING

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Many recent publications dealing with Si pulsed laser annealing have assumed that the transformation is strictly thermal melting—recrystallization. We recount observations indicating the material was not subjected to thermal melting.

In many of the recent publications dealing with the annealing of amorphous Si by pulsed (30 ps to 150 ns) lasers operating in the 1.06 to 0.26 μm wavelength region, it has been claimed that the annealing transformation occurs by a strictly thermal melting and recrystallization mechanism. It has been assumed: (a) that the energy of the incident photons is converted into heat in the lattice in a layer of depth given by the photon absorption length, and in a time small compared to the duration of the pulse; (b) that, to obtain a good anneal, it is necessary to melt through the amorphous layer to the single crystal Si substrate; and (c) that the recrystallization process, which occurs as the material cools, is liquid phase epitaxial growth [1–4].

However, in a recent review of the subject [5], Khaibullin, who is credited with the discovery of pulsed laser annealing, concluded “The mechanism of laser annealing is not yet finally established. But even now one can state that in the case of the nanosecond regimes one cannot reduce it to the ordinary thermal effect. Different factors such as photoionization, impact wave, powerful light fields etc. play a significant role”. Two particularly convincing reasons were given for dismissing the melting hypothesis. First, crystal-

line order at the surface was observed by diffraction techniques to occur within 20 to 30 ns of the beginning of a 15 to 20 ns annealing pulse. If melting had occurred, then by all estimates the molten phase would have required several times this interval to recrystallize. Second, as the molten phase has a reflectivity at normal incidence that varies between 72 and 74% through the visible wavelengths whereas amorphous and crystalline Si have significantly lower reflectivities at all temperatures, an abrupt increase in the amount of radiation reflected back should have been observed as soon as the sample surface had melted about one skin depth deep (about 8 nm), but this was repeatedly observed not to occur in cases where full annealing was observed. The second observation has also been made in experiments in Japan [6] and in our laboratory [7].

The simple thermal melting model is also inconsistent with at least five other observations.

(1) Let us continue on the subject of the reflectivity of the sample surface during the annealing event. In several laboratories a significant increase in the reflectivity of the surface has been observed [6–10] at wave lengths ranging from 1.06 μm to 533 nm, but not at 266 nm, for normal incidence and for both 57.5° and 45° off normal incidence. Let us consider how well the observations of this reflectivity increase

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fit the hypothesis that it is the result of the presence of a layer of ordinary molten Si at the surface of the sample. The complex index of refraction of molten Si has been measured by Shvarev et al. [11]^{#1} at 1.0, 0.7 and 0.4 μm from 57.5° off normal incidence. Auston et al. [8] reported the time resolved reflectivity at $\lambda = 0.63 \mu\text{m}$, 57.5° from the surface normal for both parallel and perpendicular polarization, R_{\parallel} and R_{\perp} , during laser annealing at 1.06 μm with 50 ns pulses. The observed values for the R_{\parallel} and R_{\perp} during the high reflectivity phase of the annealing process were $R_{\parallel}(0.63 \mu\text{m}) = 47\%$ and $R_{\perp}(0.63 \mu\text{m}) = 82\%$, respectively. The values for molten Si are $R_{\parallel}(0.7 \mu\text{m}) = 57\%$, $R_{\parallel}(0.4 \mu\text{m}) = 56\%$ and $R_{\perp}(0.7 \mu\text{m}) = 85\%$, $R_{\perp}(0.4 \mu\text{m}) = 84\%$. One might imagine several effects, including the presence of a vapor over the surface or ripples on the surface or a temperature dependence of the reflectivity, which might cause the reflectance measured during pulsed laser annealing to differ from that normally measured from molten Si. However, most of these would affect both R_{\perp} and R_{\parallel} whereas we see that the discrepancy in the former is only 2% while that of the latter is 20%. If the temperature of the surface were affecting the measurement, then at the end, just before recrystallization, the reflectivity should have risen to the normal value for molten Si at the melting point.

When one considers the time dependence of the reflectivity, two qualitative discrepancies between the data and the thermal melting hypothesis are evident. At the beginning of the high reflectivity phase, both Auston et al. [8] and Hodgson et al. [7] observed that the reflectivity increase occurred near the peaks of their pulses at the lowest power for which it was observed. (The rise was quite abrupt and moved out of the leading edge of the pulse as the net pulse energy was increased.) If the reflectivity increase were due to the presence of a molten layer, or due to any process that simply involved heating the surface layer to a high temperature, then this increase would have occurred well down the trailing edge of the pulse at the lowest total energies. This is obvious if one considers the case of a square wave pulse for which the maximal temperature must always occur at the end of the

pulse. One can easily prove that the maximal temperature can never occur at the peak or leading edge for any shaped pulse. The exact time of the maximal surface temperature depends on pulse duration, thermal diffusivity (which is generally T dependent), pulse shape, and extinction coefficient of the laser light. In general, the shorter the pulse duration, the squarer the pulse shape, or the lower the thermal diffusivity, the farther out of the trailing edge the maximal temperature occurs. This is because less of the integrated absorbed laser power diffuses away. Using the diffusivity of heat in Si measured under furnace conditions, one finds^{#2} that for the conditions of Auston et al.'s experiment [8,9] the onset of melting for a minimum energy pulse that melts one skin depth deep would occur 30 to 40 ns after the peak of their 25 ns HWHM gaussian pulse rather than within experimental error (less than 5 ns) of the peak. One may force the onset of the reflectivity rise to agree with experiment by adjusting the assumed value of the diffusivity of whatever it is that causes the reflectivity to rise at a critical density. In order to bring the calculated position of the reflectivity rise into agreement with experiment, one must assume the diffusivity is at least two orders of magnitude larger, e.g. 18 cm^2/s , the ambipolar diffusivity of a plasma in Si at room temperature [13], instead of 0.117 cm^2/s , the thermal diffusivity at the melting point [14,15].

When the reflectivity decreases back to values appropriate to normal single crystal Si, this should, according to the melting hypothesis, occur in a time less than 5 ns. (The skin depth is less than 10 nm and estimates of the recrystallization rate range [1-3] from 2.5 m/s to 4.5 m/s and even higher.) However, the observation, for example fig. 1 of the reports by Auston et al. [8,9] is that the duration of this transition is about 100 ns. Although Auston et al. [8] were sampling a spot centered in their annealed region and containing less than 1% its area, one might suggest that inhomogeneity in the laser beam caused the material to melt much deeper in some places than in others and that this might explain the slow decay of the reflectance. Such an effect would have produced a

^{#1} Cf., e.g., Stratton [12] for the relation between complex index of refraction and reflectivity of a metallic surface off normal incidence.

^{#2} We are grateful to G.J. Lasher for providing the computer simulation code used to establish this point. A similar conclusion for somewhat different laser annealing conditions is drawn from fig. 3 of Baeri et al. [2].

rough surface with uneven dopant concentration both laterally and vertically. Good quality material does not show this [16].

(2) Consider now the mechanical forces that must act on the surface layer if it were to melt. Suppose that an amorphous layer 100 nm thick were to be heated to the melting point, 1400°C, in 10 ns. The outward acceleration due to thermal expansion [17] ($\alpha = 4 \times 10^{-6}/^\circ\text{C}$) would be $5.6 \times 10^8 \text{ cm/s}^2 = 6 \times 10^5 G$. If this layer were to melt in the next 10 ns, then, due to the 15% contraction upon melting^{†3}, there must be a snap-back force and an acceleration back towards the substrate if the molten layer is not to fly off. If this contraction were three-dimensional (as seems to us most likely) then that acceleration would be $5 \times 10^6 G$, but this would require that the surface breakup into an array of small molten drops, which would seem inconsistent with the surface morphology flat to within 5 nm found by various authors after annealing. If, in order to account for this morphology, we assume the contraction to be one dimensional, then the snap-back acceleration must be $1.5 \times 10^7 G$. The only source of such a snap-back force that we can imagine is the surface tension of the molten phase, but the surface tension acts only in the plane of the surface. Surface tension can only hold the liquid in contact with the substrate in places where the liquid is "balled up" so that the surface is substantially normal to the substrate and extends down to it. But this would not produce the very flat annealed region that is observed.

(3) Von Gutfeld and Tsu [21] have measured the thermoelastic waves produced by the incident laser beam on the free surface of the Si during the pulsed laser annealing event as a function of incident energy. These waves were detected by a 20 MHz \pm 25% contact transducer attached to the opposite face of the Si wafer. The elastic signal is observed to rise smoothly with increasing incident energy density. There is no discontinuity at the threshold for single shot annealing nor in the range in which good quality material is obtained. There is a sharp discontinuity at higher powers

^{†3} Van Vechten [18, especially p. 1491] deduced this value from the Clapeyron equation, the entropy of fusion of Hultgren et al. [19] and the phase diagram of Bundy [20]. A value of 10%, based on an old volumetric measurement, is sometimes quoted, but we regard this value as less reliable due to experimental difficulties with molten Si.

for which surface damage and evidence of Si evaporation are observed. This discontinuity is not unlike that observed by McClland and Kniseley [22] at the point where Ge was melted with a chopped CW laser. These observations of von Gutfeld and Tsu are consistent with crystallization without thermal melting and the concomitant volume contraction. Further experiments are in progress to calibrate and elaborate this thermoelastic technique.

(4) Baeri et al. [23] have irradiated Cu-implanted Si crystals with Q-switched ruby laser single pulses. After irradiation at an energy density in excess of 1 J/cm², Cu was found to accumulate at the surface. Baeri et al. argue that accumulation of Cu atoms is a consequence of surface layer melting and resolidification, the redistribution being related to the low value (4×10^{-4}) of the segregation coefficient of Cu. Similar arguments were put forward by Cullis et al. [24], who observed redistribution of Ga and by White et al. [25], for Cu and Fe. However, in the last case Fe was found to segregate to the surface less than Cu although the redistribution coefficient of Fe is smaller.

Hoonhout and Saris [26] have made a systematic investigation of this effect for eight common dopants in Si with redistribution coefficients ranging from 0.33 to 10^{-8} . Their results show that, under implantation and pulsed laser annealing conditions similar to those of Baeri et al. [23], there is no correlation between the observation of dopant redistribution and the normal thermal redistribution coefficient. Bi, which has a redistribution coefficient $k_0 = 7 \times 10^{-4}$ similar to that of Cu, does not segregate as much as Cu. Se and Te ($k_0 = 10^{-8}$ and 8×10^{-6} , respectively) are observed to segregate even less. Assuming that impurities are frozen in because the liquid-solid interface moves to the surface faster than the impurities, one would still predict those impurities which have the lowest redistribution coefficient to segregate most. Yet this is not observed, whereas liquid-phase diffusivities for these impurities do not vary by more than one order of magnitude. Hence, surface segregation cannot be used as evidence for the thermal melting model.

(5) The fact that the "Heating 5" computer simulation code [1] of Oak Ridge National Laboratory gives a reasonable fit to the redistribution data for a number of cases actually militates against the melting hypothesis because this code neglects five large effects which would greatly increase the calculated redistribution if

included. (Actually, for the specific case presented in ref. [1], Heating 5 has already overestimated the redistribution. It was calculated that the doped layer would remain molten for 250 ns, whereas the distribution data was fit by assuming it was molten for only 180 ns.) The five effects neglected by Heating 5 are as follows: (1) As shown by van Gurp et al. [27], the molten layer should become turbulent in times short compared with the calculated persistence of the molten phase. The Heating 5 calculation assumed there was no turbulence. Turbulence will greatly increase the redistribution of elements within the molten layer and also produce lateral inhomogeneities. (2) The impurity diffusivity, $D^I(I)$, is assumed constant and equal to that measured at the melting point of pure Si, T^F , although the calculation shows the temperature of the liquid going 1400 K above T^F . It is known that liquid state diffusivities are temperature dependent [28] and usually well described by an activation energy, $\Delta H_m(I)$, of order 0.5 eV. Therefore, an order of magnitude increase in the effective $D^I(I)$ should have been assumed. (3) In fact the initial material is not single crystal but is amorphous and thus possesses an excess heat of recrystallization $\Delta H^R(Si)$ which has been estimated by Turnbull [29] to be

$$1/3 \Delta H^F(Si) = \Delta H^R(Si) > 0.5 (T^F - 300 \text{ K}) C_p,$$

where ΔH^F and T^F are the heat and temperature of fusion and C_p is the specific heat. This effect lowers the energy required to melt the damaged layer by an amount about half as large as that required to raise the temperature of an equivalent mass of pure single crystal Si to its melting point. The material should melt sooner and deeper than calculated. (4) The suppression of T^F due to the impurity I was neglected. The magnitude of the suppression of the equilibrium freezing point $T^F(Si, I, X)$ for an impurity concentration, X , can be found in the literature [30] up to the normal (equilibrium) saturation value X_s . Most values, e.g. for I = As, are

$$T^F(Si) - T^F(Si, I, X_s) \approx 200 \text{ K}.$$

However, much of the empirical data being fit are for concentrations grossly in excess of normal saturation, $X \gg X_s$. For example in the case of I = B, $X = 10^4 X_s$ is reported. In this circumstance $T^F(Si) - T^F(Si, I, X_s)$ is certainly very large and would require a detailed knowledge of the kinetics of the particular reaction to

determine. The material would melt sooner and stay molten longer than Heating 5 would calculate. (5) The degree of supercooling required to make the material recrystallize at the very large rate (about 200 cm/s) assumed is very large. In view of the considerations just mentioned, no rigorous estimate of this effect can be made. However, one could note that float zone or Czochralski Si is normally grown at about 3 mm/min = 5×10^{-3} cm/s with about 0.5 K of supercooling [31].

In conclusion, although we do not doubt that it is possible to melt Si with a laser pulse, we claim that those annealed samples having the remarkably high crystallographic and morphological quality are probably obtained by pulsed laser annealing via a nonthermal process in which thermal gradients are mild at least at the time that rapid atomic motion ceases. We believe that a realistic description of pulsed laser annealing must take account of the dense plasma produced by the absorption of the light. This will be discussed in the accompanying paper [32].

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