MELTING OF CRYSTALLINE AND AMORPHOUS SILICON BY RUBY, XeCl AND KrF LASER IRRADIATION


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MELTING OF CRYSTALLINE AND AMORPHOUS SILICON BY RUBY, XeCl AND KrF LASER IRRADIATION

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Abstract - Pulses of radiation from a ruby laser (\(\lambda = 693\) nm, FWHM = 12 ns), an XeCl excimer laser (\(\lambda = 308\) nm, FWHM = 25 and 70 ns), and a KrF excimer laser (\(\lambda = 248\) nm, FWHM = 32 ns) have been used to induce melting of crystalline silicon and thin (< 1 \(\mu\)m) amorphous layers of Si on crystalline silicon substrates. Depths of melting in crystalline Si were measured by TEM observations of the removal of dislocation loops created by low-dose ion implantation. Depths of melting of amorphous Si layers were monitored by observing the boundaries between a large polycrystalline region, assumed to form by normal melting from and resolidification back to the free surface, and a fine polycrystalline region, assumed to form by the explosive propagation inward of a thin buried liquid layer. In this work we report the comparison of predictions of heat flow calculations to the measured depth of melting in both crystalline and amorphous silicon. Excellent agreement is found with the Ruby and the XeCl results. Reasonable agreement with the KrF results is obtained only if the silicon liquid phase reflectivity at 249 nm is significantly less than that obtained by extrapolation of the optical parameters from longer wavelengths.

I - INTRODUCTION

It is now well established that pulsed lasers remove ion implantation damage in semiconductors by melting the amorphous layer created by the implantation. Usually this occurs by nucleation of a liquid film at the free surface and inward propagation of the liquid-amorphous interface, in a manner typical of other first order phase transformations. If enough laser energy is supplied to melt through the amorphous layer and through the defective crystal adjacent to the amorphous layer, the underlying crystalline substrate provides a seed for high quality epitaxial crystal growth. If the energy is sufficient to melt only partway through the amorphous layer, several interesting effects have been observed, including "epitaxial" growth of amorphous silicon (a-Si) /1/, explosive crystallization of the unmelted a-Si /2,3/, and nucleation of crystalline /4/ or amorphous /1/ Si at or near the free surface.

In this paper we compare a heat-flow program's numerical calculations of the maximum depth melted by pulsed laser irradiation to TEM observations on irradiated a-Si and crystalline Si (c-Si). Ion implantation species, doses and temperatures were controlled in order to produce lightly damaged c-Si containing only dislocation loops or layers of fully amorphous Si on the crystalline substrate. From microstructural changes observed after irradiation with Ruby /3/, XeCl /5/, and KrF /6/ laser pulses the depth of melting was determined. The measured melt depths are compared to heat flow calculations.

II - EXPERIMENT

Silicon single crystals having (100) orientation were implanted with \(^{30}\)Si\(^{+}\) ions (200 keV, 1.5 x 10\(^{16}\)/cm\(^{2}\), liquid nitrogen (LN\(_2\)) temperature) to create an a-Si layer approximately 5000 Angstroms thick. Some of these samples were again implanted with
350 keV $^{30}$Si$^{+}$ ions ($2.0 \times 10^{16}$/cm$^2$, LN$_2$) to extend the a-Si thickness to 7660 Å. Other single crystals of Si were implanted with 175 keV $^{30}$Si$^{+}$ ions to a dose of only $2.0 \times 10^{14}$/cm$^2$, at room temperature. This implant created dislocation loops distributed to a depth of roughly 4500 Å, but no a-Si. Likewise, dislocation loops distributed to a depth of roughly 7000 Å was created by a multiple-energy implantation of $^{18}$B$^+$ ions (25 keV, $1.7 \times 10^{15}$/cm$^2$; 50 keV, $2.5 \times 10^{15}$/cm$^2$; 100 keV, $3.5 \times 10^{15}$/cm$^2$; 200 keV, $4.65 \times 10^{15}$/cm$^2$, room temperature) into single crystals of (111) Si. The specimens were irradiated with single pulses from a ruby laser ($\lambda = 693$ nm, FWHM = 12 ns), a XeCl excimer laser ($\lambda = 308$ nm, FWHM = 25 and 70 ns), and a KrF excimer laser ($\lambda = 248$ nm, FWHM = 32 ns). Microstructural changes following irradiation were observed by cross section transmission electron microscopy. The details of the experiments are reported elsewhere /3,5,6/.

Table I. Thermophysical and optical parameters used in heat flow calculations.

<table>
<thead>
<tr>
<th></th>
<th>LIQUID</th>
<th>AMORPHOUS</th>
<th>CRYSTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity (W/cm/K)</td>
<td>1.4</td>
<td>0.026/7/</td>
<td>1585 $\times 1.229$, $T &lt; 1371$ K/8/</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.221, $T &gt; 1371$ K</td>
</tr>
<tr>
<td>Specific Heat (J/cm$^3$/K)/9/</td>
<td>2.56</td>
<td>(1.988 + 3.54 $\times 10^{-4}$ $T - 3.68 \times 10^4$ $T^{-2}$)</td>
<td></td>
</tr>
<tr>
<td>Melting Temperature (K)</td>
<td>-</td>
<td>1485/2/</td>
<td>1685</td>
</tr>
<tr>
<td>Latent Heat of Melting (J/cm$^3$)</td>
<td>-</td>
<td>2986/10/</td>
<td>4200</td>
</tr>
<tr>
<td>Reflectivity:/11/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>693 nm</td>
<td>0.739</td>
<td>0.414</td>
<td>0.336</td>
</tr>
<tr>
<td>308 nm</td>
<td>0.734</td>
<td>0.562</td>
<td>0.587</td>
</tr>
<tr>
<td>248 nm/12/</td>
<td>0.65</td>
<td>0.585</td>
<td>0.65</td>
</tr>
<tr>
<td>Absorption Coeff. (10$^6$/cm):/11/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>693 nm</td>
<td>1.01</td>
<td>0.1</td>
<td>0.00134 exp(T/427 K)</td>
</tr>
<tr>
<td>308 nm</td>
<td>1.53</td>
<td>1.38</td>
<td>1.48</td>
</tr>
<tr>
<td>248 nm</td>
<td>1.76</td>
<td>1.40</td>
<td>1.70</td>
</tr>
</tbody>
</table>

A heat-flow program written by M. O. Thompson was used to calculate the depth of melting into a-Si and c-Si as a function of pulse energy density. The program is a finite-element numerical solution of the heat-flow equation with the boundary condition that the temperature of the liquid-crystal interface is fixed at the melting point of c-Si and the temperature of the liquid-amorphous interface is fixed at the melting point of a-Si, which was chosen to be 200 K below that of c-Si. For the ruby and XeCl lasers, the measured temporal laser pulse profiles were digitized and inserted into the calculations. The measured KrF pulse from a laser identical to that used in the experiment was used for the KrF calculations. The thermophysical and optical parameters used in the calculations for the three phases of Si are listed in Table I.

III - RESULTS

In Fig. 1 are shown typical TEM results from irradiation of a-Si layers. The top layer of large polycrystalline (LP) Si has been shown to form by normal melting of a-Si initiating from and returning to the free surface. Between it and any remaining a-Si is a layer of fine polycrystals (FP) /13,14/ which have been shown to form by explosive crystallization, i.e. the formation and inward propagation of a thin buried liquid layer /2,3/. The explosive behavior is driven by the difference in melting points of c-Si and a-Si and is sustained by the difference in the latent heats of fusion of the two phases. Between any remaining amorphous material and the single crystal substrate is seen a dark band of dislocation loops formed during ion implantation. Sharp boundaries between the LP and FP regions and between the FP and the underlying amorphous layers are clearly visible.
Fig. 1. Cross-section TEM micrographs of $^{30}\text{Si}^+\text{-implanted}$, 7660-Å thick a-Si layers after pulsed KrF irradiation with the following energy density: (a) 0.5, (b) 0.8, (c) 1.0, and (d) 1.2 J/cm².

Fig. 2 shows typical results on melting of crystalline Si. The top 3000 Å of Si is free of dislocation loops. The loops present from 3000 to 4500 Å depth are of the same density as in the as-implanted material. The removal of dislocations loops provided evidence for melting; thus the loops serve as markers to determine the depth of melting.

Fig. 2. Cross-section TEM micrograph from light-dose $^{30}\text{Si}^+\text{-implanted}$ (100) Si after pulsed KrF irradiation with 1.4 J/cm².
In Fig. 3 we plot the depth of melting into a 5000 Å thick a-Si layer as a function of ruby pulse energy density. The total thickness of the FP and LP regions shows a rapid initial increase with pulse energy density followed by a saturation at the original a-Si layer thickness. However, the thickness of the LP region alone exhibits a linear increase with pulse energy density, and is in excellent agreement with the calculated maximum melt depth. The correspondence between calculated maximum melt depth and observed LP thickness was used, along with the observed redistribution of implanted As, In, and Cu, to deduce that the LP region forms by normal melting of a-Si and that as it is regrowing by the motion of a crystal-liquid interface back towards the surface, the FP region forms by the inward propagation of a buried liquid layer /1/.

![Pulsed Ruby Laser Graph](image)

**Fig. 3.** Thickness of (FP + LP) and LP regions in 5000 Å thick a-Si layer as a function of ruby pulse energy density. The filled circles show the calculated maximum melt depth.

In Fig. 4 we plot the observed and calculated depth of melting of crystalline Si (11B+ implanted) as a function of pulse energy density for 25 ns and 70 ns XeCl laser pulses. Again, we see that the melting threshold, the linear dependence upon energy and the inverse relationship to pulse duration is correctly predicted. The liquid phase reflectivity was obtained from Jellison's extrapolation /11/ of the optical constants measured by Shvarev et al., /15/ at longer wavelengths. Although Jellison advises caution in the use of the extrapolation, it appears quite valid down to wavelengths of 308 nm.

![XeCl Laser Graph](image)

**Fig. 4.** Measured and calculated dependence of depth of melting of c-Si on pulse energy density for 25 and 70 ns XeCl irradiation.
In Fig. 5, we plot the observed and calculated depth of melting of crystalline Si (30Si⁺-implanted) and a-Si (7660 Å thick) as a function of KrF pulse energy density. The solid line corresponds to the calculation for a liquid-phase reflectivity of $R_L = 0.65$, as suggested by recent results of Fogarassy et al., /12/. Although the melting thresholds of c-Si and a-Si appear to be correctly predicted, the calculated melt depths fall approximately 15% below the measurements for melting of a-Si. The sensitivity to $R_L$ is demonstrated by the dashed lines, for which the value of 0.75, obtained by Jellison's extrapolation /11/, was used. The agreement with experiment for both a-Si and c-Si is very poor if $R_L$ is assumed to be 0.75. Note that for the ruby and XeCl wavelengths, we had much more success using values thus tabulated by Jellison. Although it is not the purpose of this work to adjust thermophysical and optical parameters until good agreement between calculated and observed melting behavior is observed, we note that a slightly smaller value of $R_L$ than that suggested by Fogarassy et al., could not reconcile the calculations to the observations for melting of both the crystal and the amorphous phases. In addition, a 50% reduction in the thermal conductivity of a-Si increases our calculated melt depths by no more than 200 Å. We believe the most likely source of the observed discrepancy to be uncertainties in the experimental energy calibration and pulse shape.

**IV - CONCLUSIONS**

Depths of pulsed laser melting of crystalline Si were monitored by TEM observations of the removal of dislocation loops created by ion implantation. Depths of melting of a-Si layers were monitored by observing the boundaries between a large polycrystalline region, assumed to form by normal melting from and resolidification back to the free surface, and a fine polycrystalline region, assumed to form by the explosive propagation inward of a thin buried liquid layer. Heat-flow calculations yield excellent agreement with the observations for pulsed ruby melting of a-Si, XeCl melting of c-Si and KrF melting of c-Si. The calculated melt depth is roughly 15% lower than the observed melt depths of KrF pulses on a-Si. Extrapolation of the wavelength dependence of the optical constants of liquid Si down to 308 nm yields a value of $R_L$ that, when used in the heat-flow calculations, reproduces the data quite well. However, further extrapolation to 248 nm produces results that do not match the data at all. Reasonable agreement is obtained with the use of the significantly lower liquid phase reflectivity of 0.65. Similar conclusions regarding the value of the liquid phase reflectivity at 248 nm have been reported by Fogarassy et al.
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