

## Phase Transitions in Amorphous Si Produced by Rapid Heating

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Amorphous Si layers have been melted by pulsed electron irradiation. Implanted As has been used as a marker for determining melt duration. Systematic differences between As diffusion in initially amorphous or crystalline Si are interpreted in terms of different enthalpies of melting between amorphous (1220 J/g) and crystalline (1790 J/g) Si. The implanted amorphous layers melt and crystallize at significantly lower electron energies than those required to melt and recrystallize crystalline Si, indicating that amorphous Si melts at 1170 K compared to 1685 K for crystalline Si.

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Recently Bagley and Chen<sup>1</sup> and Spaepen and Turnbull<sup>2</sup> have examined the thermodynamic properties of amorphous and single-crystal Si and Ge. They estimate the melting temperatures and enthalpies of melting of the amorphous semiconductor to be approximately 25% lower than the crystalline values. The melting temperature ( $T_{i,a}$ ) of amorphous Si could then be 400 K lower than the crystal value ( $T_{i,c}$ ) of 1685 K. This behavior is a consequence of the higher free energy of the amorphous state. The advent of nanosecond pulsed heating techniques, such as laser- or electron-beam irradiation, has made it possible to investigate this intriguing melting and recrystallization behavior. We have used pulses of electrons<sup>3</sup> because the coupling between the incident beam and irradiated samples is independent of the physical state (amorphous, crystal, or liquid) of the semiconductor. Our experimental configuration of an electron beam of average energy 10 keV, incident at a glancing incidence to the Si surface ensures that nearly all the energy is deposited in the outermost 1  $\mu\text{m}$  of material. Heat-flow calculations show that the temperature gradient over the first 2000  $\text{\AA}$  during the irradiation is less than 50 K. This thermal behavior should be contrasted with laser irradiation<sup>4</sup> where gradients of 500 K can be generated over 2000  $\text{\AA}$  due to the enhancement of the absorption coefficient in the molten silicon.

We have used the combined techniques of ion implantation, Rutherford backscattering and channeling, and transmission electron microscopy to investigate the melting and recrystallization of amorphous and single-crystal surface layers. Arsenic was implanted in Si and used as a marker

to show the duration of the melt. The diffusivity<sup>5</sup> of As in molten Si is  $2 \times 10^{-4} \text{ cm}^2/\text{sec}$  as compared to its highest solid-state diffusivity of  $10^{-12} \text{ cm}^2/\text{sec}$ . The position of the implanted As can be measured with Rutherford backscattering with a depth resolution of approximately 100  $\text{\AA}$ . The threshold for melting can therefore be measured with some accuracy. Arsenic was implanted in  $\langle 100 \rangle$  Si wafers at a dose of  $10^{16}/\text{cm}^2$  and energy of 50 keV. The wafers were then fully annealed in a furnace at a temperature of 900  $^\circ\text{C}$  for 30 min. Channeling measurements showed that crystallinity was restored and As was incorporated on lattice sites. Some of these As implanted wafers were then implanted with multiple-energy (90, 110, and 130 keV) P implants, to a total dose of  $9 \times 10^{15}/\text{cm}^2$ , to produce a uniform surface amorphous layer 1900  $\text{\AA}$  thick, as measured by channeling and backscattering.

Sets of wafers with crystalline and amorphous surfaces were then irradiated with a pulsed electron beam<sup>3</sup> of average diameter 5 cm in the energy range from 0.42–1.3 J/cm<sup>2</sup> in eight steps of approximately 0.1 J/cm<sup>2</sup>. At each step the crystalline and amorphous surfaces were irradiated with nominally the same energy. The electron pulse has a full width at half maximum of approximately 50 nsec. Below 0.55 J/cm<sup>2</sup> no motion of As was observed. Above this value As diffused in both the initially amorphized and single-crystal surfaces. Greater motion occurred, however, in the initially amorphized layer. The difference in As movement between the amorphized and surface crystal samples becomes progressively smaller with increasing energy deposition. Figure 1 (left-hand side) shows the experimentally

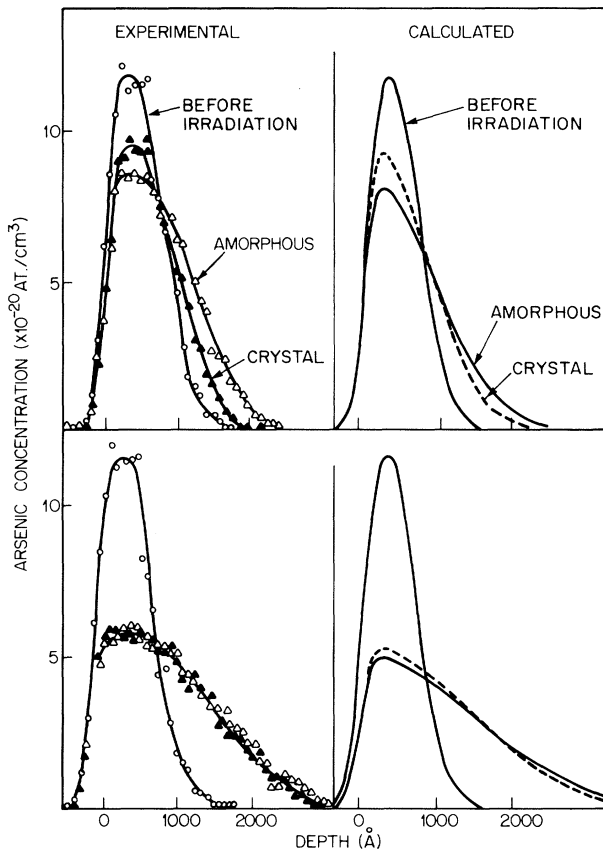


FIG. 1. Experimental (left-hand side) and calculated (right-hand side) As depth profiles for the initially crystalline and amorphized samples after electron irradiation of 0.65 (upper) and 1.1 (lower)  $J/cm^2$ , respectively.

measured As profiles after irradiation at energies of 0.65 and 1.1  $J/cm^2$ , respectively.

We have calculated Si melting and As diffusion from heat-flow calculations<sup>4</sup> by using crystalline Si thermodynamic properties as starting parameters. We assume<sup>5</sup> a constant specific heat of 0.95  $J/g \cdot K$ , enthalpy of melting  $\Delta H_{lc}$  of 1790  $J/g$ ,  $T_{lc}$  of 1685 K and a temperature dependent thermal conductivity smoothly ranging from 1.45  $W/cm \cdot K$  at 300 K to 0.2  $W/cm \cdot K$  at  $T_{lc}$ . The calculated temporal and spatial behavior of temperature in the surface layer depend on the energy deposition profile of the electron beam. Direct measurements of this profile do not exist but estimates have been made with use of Monte Carlo simulation.<sup>3</sup> We used the previously reported shapes of the deposition profile of the electron beam<sup>3</sup> but adjusted the characteristic depths to fit the experimental data of the As diffusion in the single-crystal specimens. From the time

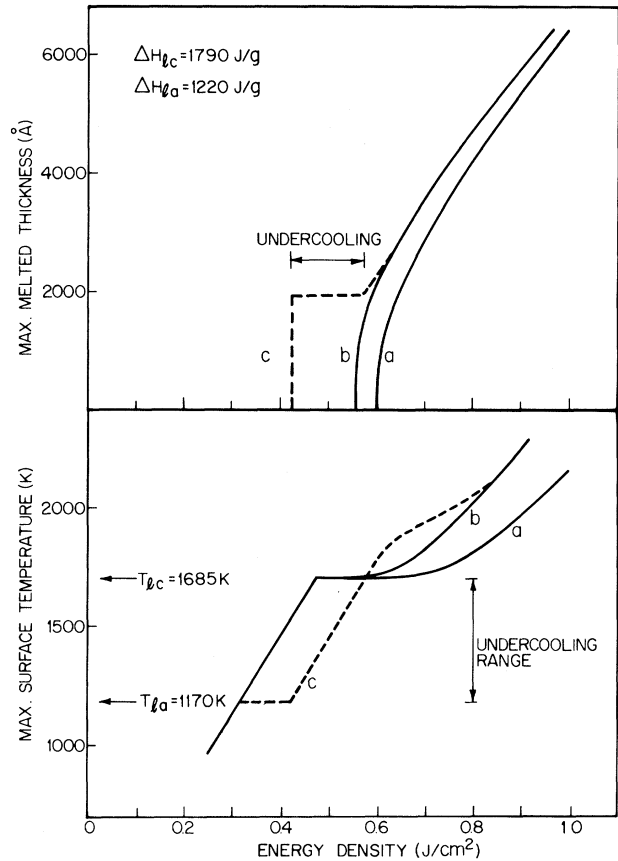


FIG. 2. Calculated maximum melt-front penetration (upper) and maximum surface temperature (lower) as function of electron-energy density (curve *a*) for a single-crystal sample, and (curve *b*) for a 1900-Å amorphous layer in crystal sample assuming  $\Delta H_{la} = 1220 J/g$  and  $T_{la} = T_{lc}$  and (curve *c*) assuming  $\Delta H_{la} = 1220 J/g$  and  $T_{la} = 1170 K$ .

evolution of the melt front, the corresponding As diffusion profiles can be calculated<sup>7</sup> and they are shown on the right-hand side of Fig. 1.

Figure 2 shows some of the results of the heat flow calculations. Curve *a*, in the upper part of the figure, gives the calculated maximum thickness of the melt depth for crystalline Si as a function of electron-energy density. Curve *b* shows the maximum melt depth for a 1900 Å amorphous layer on crystalline Si. In this calculation to fit the As profiles, we take the enthalpy of melting of amorphous Si,  $\Delta H_{la}$ , to be 1220  $J/g$ , which is 32% lower than the crystalline enthalpy. We have assumed the same specific heats and temperatures of melting for the amorphous and crystalline phases. The calculation for the As diffusion profiles are shown on the right-hand side of Fig. 1.

It is important to emphasize that once we assume that the specific heats are independent of the state of the Si and that melting penetrates the amorphous layer to the underlying crystal, the value we obtain for  $\Delta H_{ia}$  will be independent of the actual melting temperature of amorphous Si. The observation of greater As diffusion in the initially amorphized sample depends only on the reduced enthalpy of melting of the amorphous phase. By fitting the broadening of the As diffusion profiles in the crystal and amorphous samples, we calculate the difference in the enthalpy of melting between crystal and amorphous Si to be  $570 \pm 60$  J/g. This error arises from the fits to the backscattering spectra. However, we do not know the energy reproducibility of the beam to better than 10%. We therefore conclude that the enthalpy of melting of amorphous Si is  $1220 \pm 150$  J/g.

Several features of the calculations need to be considered. We assumed the specific heat of Si to be temperature and phase independent. Data for amorphous Si do not exist but Chen and Turnbull<sup>8</sup> showed that for amorphous Ge the specific heat is 5% greater at room temperature and 15% greater when extrapolated to the melting temperature. If we assume, therefore, on average, that the specific heat of amorphous Si is 10% greater than crystal Si, a  $\Delta H_{ia}$  value of 1150 J/g is required to fit the diffusion data. The specific heat of liquid metallic Si may be 10% lower than the crystalline value at  $T_{ic}$ .<sup>9</sup> If we assume a similar behavior for the molten amorphous Si, the value which we obtain for  $\Delta H_{ia}$  from the As diffusion profiles will depend weakly on the choice of  $T_{ia}$ . For  $T_{ia} = 1170$  K, a  $\Delta H_{ia}$  value of 1280 J/g is required to fit the diffusion data. However, these uncertainties, introduced by our lack of knowledge of specific heats, are not as significant as the errors of  $\pm 150$  J/g introduced by experimental uncertainties in the energy deposited by the electron beam.

If the input energy is not sufficient to melt the surface amorphous layer and a part of the underlying crystal, the resulting melting and recrystallization phenomena will be crucially dependent upon the value of  $T_{ia}$ . To illustrate this point, curve *c* in the upper part of Fig. 2 shows the calculated melt depth for a 1900-Å amorphous layer assuming an enthalpy of melting of 1220 J/g and  $T_{ia} = 1170$  K. The amorphous layer melts at 0.42 J/cm<sup>2</sup> but the melt front does not penetrate the underlying crystal until 0.58 J/cm<sup>2</sup> is reached. Above this value the crystal melts and the melt

depth coincides with that calculated for curve *b* where  $T_{ia} = T_{ic}$ . The lower part of Fig. 2 shows the calculations for the maximum surface temperatures.

The following phenomena are observed for irradiation energies below 0.55 J/cm<sup>2</sup>. No As motion is observed for crystalline Si and we infer that the crystalline Si has not melted. No dopant motion occurs for the amorphous Si either. However, the following recrystallization phenomena were observed. In the range 0.42–0.5 J/cm<sup>2</sup>, epitaxial regrowth occurs with the interface moving between 500 and 1000 Å. Within this range, the interface motion does not depend upon incident energy. Figure 3 shows transmission electron microscopy (TEM) micrographs of cross-sectioned samples. The upper micrograph shows the 1900-Å amorphous Si layer (A) with the presence of defects at the interface (marked by the arrow) resulting from the implantation. The middle micrograph shows the structure following an irradiation of 0.5 J/cm<sup>2</sup>. Epitaxial regrowth has occurred over a distance of 800 Å. However, the epitaxial layer (B) is highly defective as indicated by the high density of microtwins. The

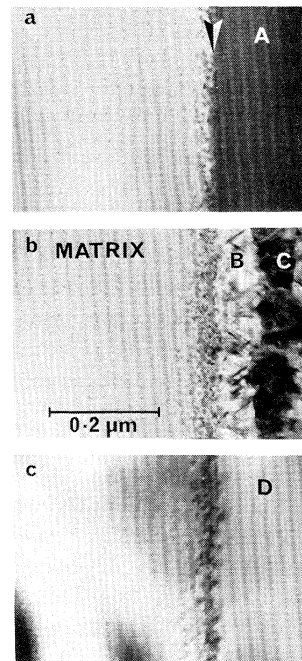


FIG. 3. TEM micrographs of cross-sectioned samples: Upper, 1900-Å amorphous layer before irradiation. Middle, irradiation of 0.5 J/cm<sup>2</sup>; note epitaxial growth from original interface to polycrystalline boundary. Bottom, irradiation of 0.55 J/cm<sup>2</sup>.

outer Si layer consists of large grain poly crystallites (C), with some spanning the thickness of the polycrystalline layer. The lower micrograph of the 0.55-J/cm<sup>2</sup> irradiation shows complete epitaxial recrystallization (D) with some defects at the interface. Above this energy, TEM shows that the surface layer is free of defects.

We believe that the structures we observe in the recrystallization of the amorphous layer are formed in the following manner. The amorphous layer melts at temperatures considerably less than  $T_{ic}$ . The undercooled melt then recrystallizes from both the single-crystal interface and random nucleation centers at the free surface. These competitive processes produce the observed layered structure. The absence of any observed As-dopant motion can therefore be explained in terms of the extremely large recrystallization velocities. If we assume the As has not diffused further than 100 Å the recrystallization velocity must be greater than 10 m/sec. This high velocity is a possible cause of the large number of defects observed in the epitaxial layer.

At 0.42 J/cm<sup>2</sup>, we have been able to detect with the cross-sectional TEM technique areas where thin layers of amorphous Si still exist at the single-crystal interface. The original amorphous layer has therefore not completely melted through to the interface. We assume that the energy threshold for melting the amorphous Si occurs at 0.42 J/cm<sup>2</sup> which corresponds to a  $T_{ia}$  of 1170 K. This threshold measurement of the melting temperature depends critically upon the energy calibration of the incident electron beam. An energy uncertainty of 10% corresponds to a temperature uncertainty of ±100 K.

We have used a pulsed electron beam to rapidly heat amorphous and single-crystal Si above the melting temperatures. From measurements of the diffusion of implanted As, we calculate the

enthalpy of melting of amorphous Si to be 1220 ± 150 J/g. This value should be contrasted with the crystalline value of 1790 J/g. Structural measurements below the threshold for melting single-crystal Si indicate that amorphous Si melts at 1170 ± 100 K as compared with the crystal melting point of 1685 K. These remarkable differences in enthalpies and melting temperatures are a manifestation of the large differences in free energy of the Si amorphous and crystalline state.

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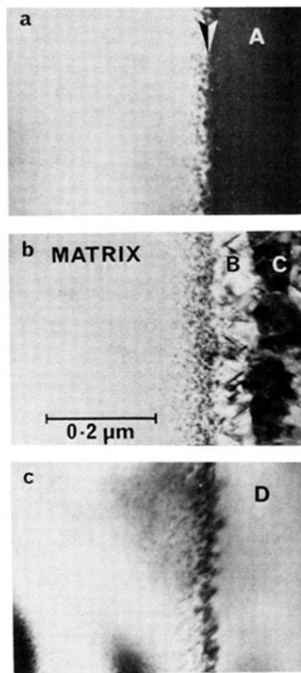


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