17.3 Laser Irradiation of Solids

Summary: Surface and sub-surface regions of solids are modified by rapid melting and quenching, using a high-powered, pulsed (30 ns) ruby laser. The main emphasis of this work is on laser annealing, epitaxy and doping of silicon. Computer programs have been developed to calculate the heat-flow which takes place during pulsed laser irradiation. From such calculations, information can be obtained about temperature profiles, melt depths, recrystallization velocities and quench rates.

17.3.1 Comparison of heat-flow simulations with other calculations and experimental results

T K Marais and R Pretorius

Calculations from the heat-flow simulation program HEATUP {1} were compared with similar calculations and experiments done by other authors. Table 1 shows the threshold laser energy density required to melt single crystal Si as determined by various experiments. The value obtained from the simulation program HEATUP is also given and the agreement with the experimental values is excellent.

Figure 1 shows the kinetics of the melt front for a 27.5 nsec laser pulse incident on a Si crystal for different laser energy densities. The continuous curves are from the HEATUP program and the broken lines from Bell's results {2}. The agreement between the two calculations is good, showing that the curves converge as the energy density is increased. In figure 2 results from the HEATUP program are compared with results obtained experimentally by the transient conductance technique {3}. The solid curve shows results from the heat-flow program and the broken lines are experimental results. Again the agreement between the computer simulation and the experimental data is good, differing only at the lower energy densities. Similar good comparisons between theory and experiments were obtained by Thompson et al. {3}.

Table 1 The threshold laser energy density required to melt Si as determined from various experiments.

Measurements	Value (J/cm^2)
Ellipsometry	1
Reflectivity	0.7
Capacities on Schottky barrier	(0.7 - 0.8)
Superficial resistance	0.75
Depth penetration of impurities	(0.75 - 0.8)
Calorimetry	0.80
HEATUP	0.79

References

1. National Accelerator Centre Annual Report NAC/AR/87-01 (CSIR, 1987) p 211

2. A E Bell, Review and Analysis of Laser Annealing, RCA Review 40 (1979) 295

3. M O Thompson and G J Galvin, Laser-Solid Interactions and Transient Thermal Processing of Materials (North-Holland, 1983) Vol 13

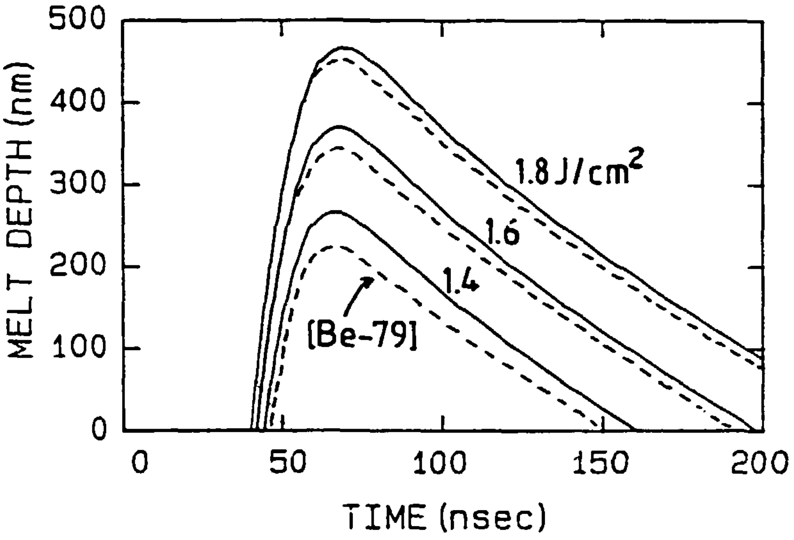

Fig. 1 Kinetics of the melt front for a 27.5 nsec laser pulse incident on a Si crystal at various laser energies. The solid lines were obtained from the HEATUP program and compared with A E Bell's {2} calculated results.

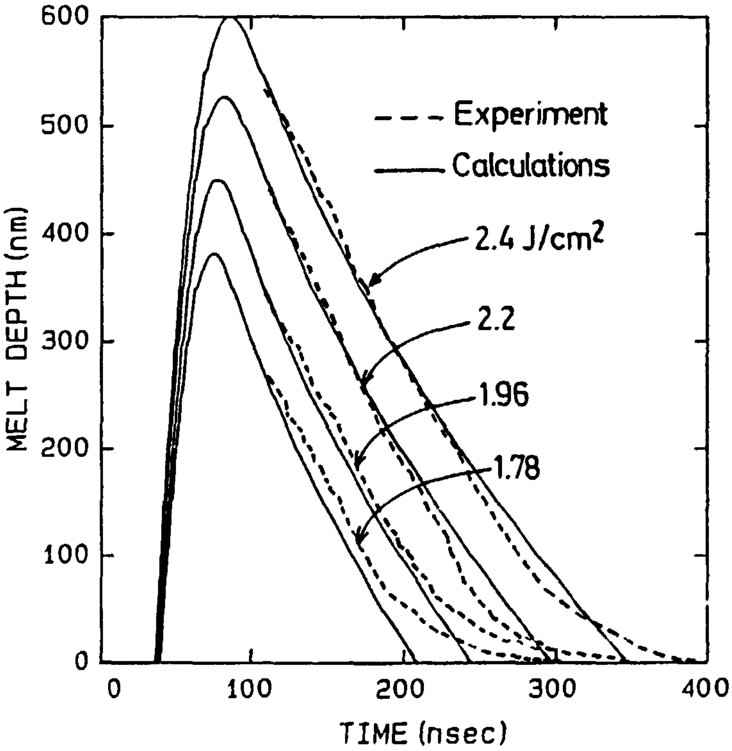

Fig. 2 Kinetics of the melt front movement for a 30 nsec ruby lase pulse incident on Si(c). The solid lines (from HEATUP program) are compared with experimental results obtained by transien electrical conductance {3}.

17.3.2 Parameters affecting recrystallization velocity during antimony doping of silicon

T K Marais, W Perold* and R Pretorius

* University of Stellenbosch

A study of the recrystallization velocity is of great importance as it determines the final microstructure of the material. A lot of effort is put into controlling this velocity since the interface velocity also has a critical influence on the dopant segregation and trapping as well as the interface stability. The computer modelling program HEATUP {1} was used to calculate the resolidification velocity as a function of the following parameters which can be controlled experimentally: (1) laser beam pulse width, (2) ambient sample temperature and (3) energy density. We investigated the regrowth velocity when a thin layer of Sb was deposited onto single crystal Si. Previous work has shown that if the regrowth velocity is greater than 15 m/sec then the irradiated area becomes amorphous in the case of single crystal Si {2}. This situation would be totally undesirable for doping of semiconductors. From figure 3 it can be seen that if the molten Si thickness is less than 170 nm, then the irradiated area regrows with velocities greater than 15 m/sec in the case of a laser pulse width of 1 nsec. In this case the irradiated region would become amorphous. This occurs because of the very sharp temperature gradient that develops at the liquid-solid interface.

The effect of the ambient temperature on the regrowth velocity is given in figure 4. When the ambient temperature is changed from 300K to 900K, the maximum regrowth velocity changes from 3 m/sec to 0.6 m/sec. This approach of controlling the ambient temperature of a sample is a excellent way of tailoring the melt front to a desired value.

Figure 5 shows the maximum regrowth velocity of Si as a function of laser energy density for a 50 nm Sb layer on Si(c). A maximum regrowth velocity is obtained at the threshold energy density required to melt the underlying Si. Thereafter the regrowth velocity decreases linearly with increase in laser energy and it can therefore be expected that more Sb would segregate to the surface.

References

1. National Accelerator Centre Annual Report NAC/AR/87-01, (CSIR, 1987) p 211

2. M O Thompson and G J Galvin, Laser-Solid Interactions and Transient Thermal Processing of Materials, Vol 13, ed J Narayan, W J Brown and R A Lemons (North-Holland, 1983)

17.3.3 The effect of Sb thickness on laser induced doping

T K Marais and R Pretorius

The computer simulation program HEATUP {1} was used to determine the thickness of melted Si as a function of the thickness of Sb deposited.

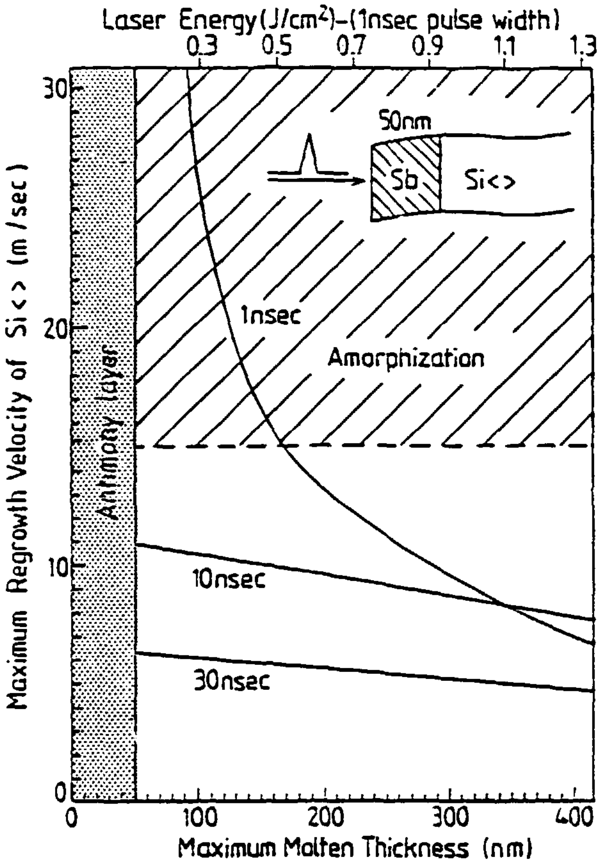

Fig. 3 Maximum regrowth velocity in Si as a function of the maximum molten Si thickness for various pulse widths. For a 1 nsec pulse width, amorphization can commence if the maximum molten thickness of Si is less than 120 nm. This corresponds to a laser energy density less than 0.5 J/cm^2. For pulse width greater than 10 nsec, amorphization will not occur.

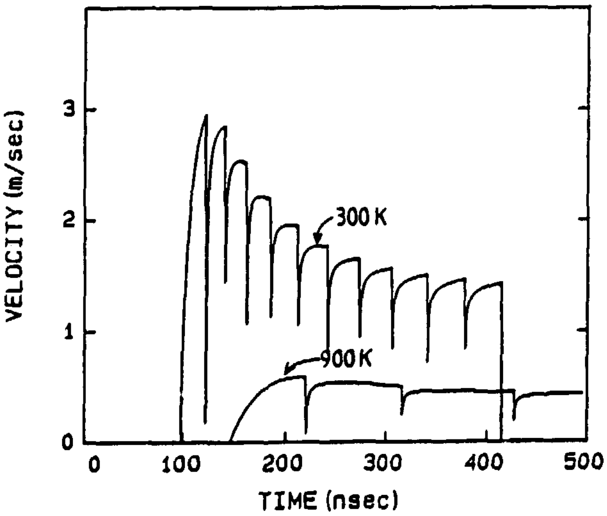

Fig. 4 Regrowth velocity of the melt front as a function of time for two ambient sample temperatures. A maximum regrowth velocity of 3 m/sec is obtained for a ambient temperature of 300K compared to only 0.6 m/sec when the temperature is 900K.

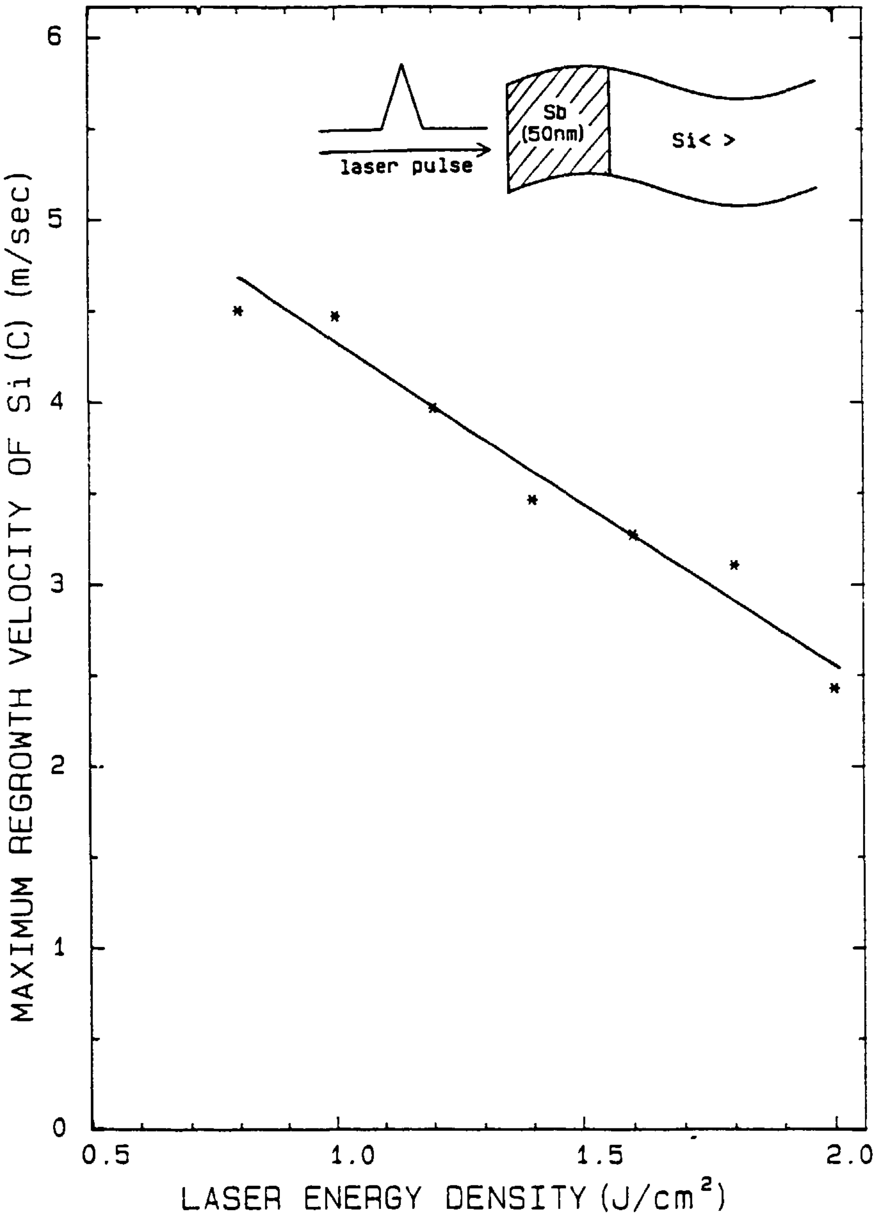

Fig. 5 Maximum regrowth velocity of Si as a function of laser energy-density for a 50 nm Sb layer on Si(c). The highest regrowth velocity is obtained at the threshold energy-density for melting the underlying Si. Thereafter there is a linear decrease in molten Si as the laser energy is increased.

These calculations were done for various Sb deposited thickness at laser energy-densities of 0.9 1.4 and 1.8 J/cm^2, respectively (see figure 6). For a laser energy of 1.8 J/cm^2, about 380 nm of Si melts when there is no Sb deposited on Si. As the Sb thickness on Si is increased, the Si melt depth increases for all three laser energies shown and reaches a maximum for Sb thicknesses in the range of 50 nm. This is probably due to the high absorption coefficient of Sb. As the Sb thickness is increased, the molten Si thickness decreases because a greater portion of the laser energy is used in heating the Sb layer. In all three cases it is found that doping of Si would not be possible for deposited thickness greater than 275, 700 and 1000 nm for the laser energies of 0.9 1.4 and 1.8 J/cm^2, respectively.

Figure 7 shows the threshold laser energy-density for melting the underlying Si as a function of Sb thickness. The solid curve was obtained by fitting a continuous line to the filled squares which represent the points at which the computer simulations were performed. The dotted line is a fit to the data obtained experimentally. The error bars incorporate only the errors in determining the threshold energy from the experimental data and not errors that can arise during the experiment itself. The agreement between the theoretical and experimental values is quite good, both going through a minimum for Sb thicknesses in the range of 20 to 50 nm.

Reference

1. National Accelerator Centre Annual Report NAC/AR/87-01 (CSIR, 1987) p 211

17.3.4 Buried dopant profiles in silicon

R J Carolissen and R Pretorius

A doped region buried in Si<100> was prepared using conventional UHV depositions onto Si<100> and laser annealing with a single-pulse (30 ns pulse width) Q-switched ruby laser equipped with a beam homogenizer.

A 1000 Å Si(a) layer, followed by a thin layer of Sb (10 to 20 Å) and finally a 2500 Å thick Si(a) layer was evaporated onto Si<100> substrates in an UHV system. The first 1000 Å of Si(a) was deposited because of the difference in melting temperatures of amorphous and crystalline silicon, thereby increasing the time that liquid state diffusion can take place behind the Sb layer. Diffusion calculations have shown that for Sb thicknesses greater than 25 Å, the Sb concentration will exceed the laser solubility limit (1.3×10^{21} atoms/cc) when resolidification occurs. The excess Sb atoms will remain as a melt thereby screening the silicon atoms in front from the underlying crystal, inhibiting alignment and subsequent epitaxial regrowth.

After irradiation in atmosphere across a range of laser energies, RBS results showed excessive oxidation in the regrown region. This was linked to void formation in the silicon that was deposited at room temperature and exposed to atmosphere prior to laser annealing. An equally important requirement for this excessive oxidation to occur

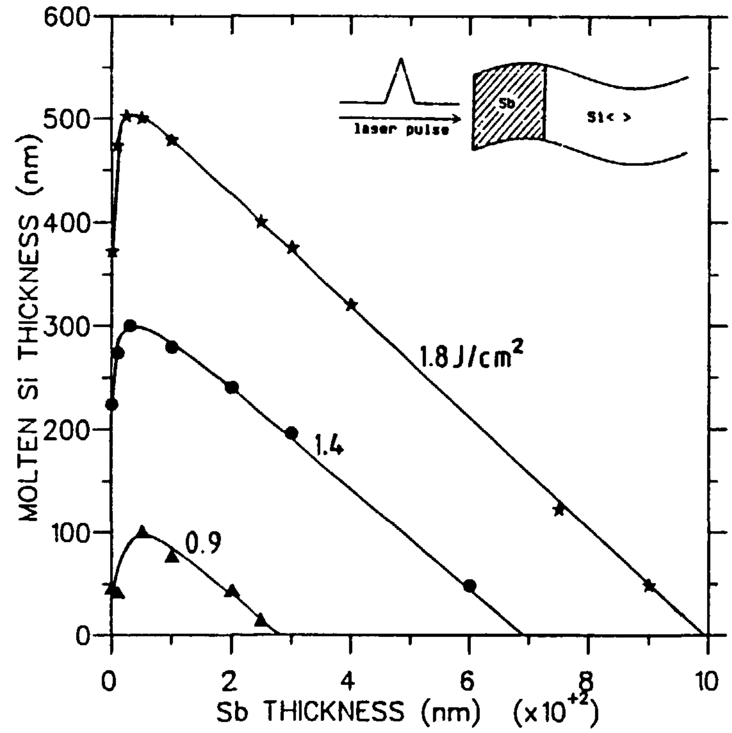

Fig. 6 Graph of molten Si thickness versus thickness of deposited Sb on Si(c) for various laser energies. For a laser energy-density of 1.8 J/cm^2, about 380 nm of Si melts when no Sb is deposited. However, for all three energies shown a maximum amount of Si is molten when the deposited thickness is about 50 nm.

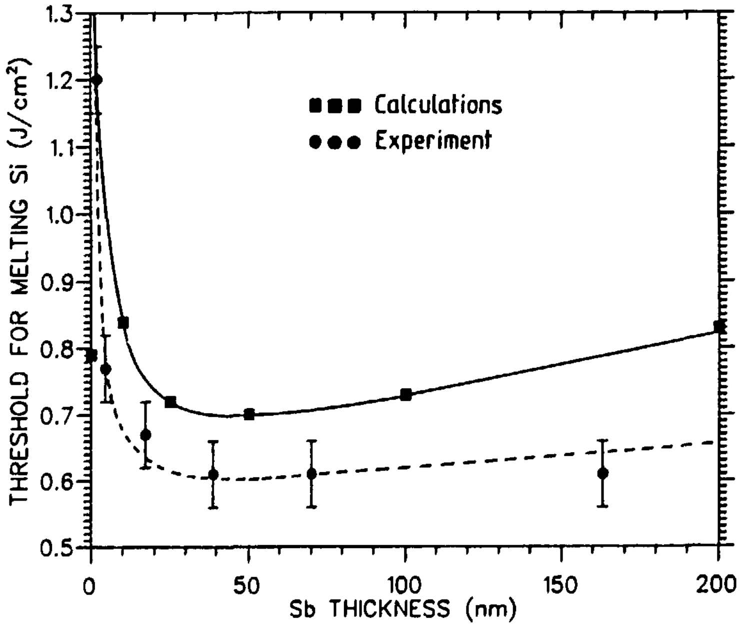

Fig. 7 Threshold energy-density for melting underlying Si as a function of Sb thickness deposited on Si(c). A laser energy-density of 0.79 J/cm^2 melts crystalline Si, however, more energy is required as soon as an Sb layer is deposited on Si. The agreement between the theoretical and experimental values is quite good.

is that high concentrations of Sb be present at the near surface region (see next section). Channelling results showed poor regrown crystal quality which can be attributed to the oxidation in this region and the porosity of the regrown silicon.

The same structure as above was deposited onto a Si<100> substrate maintained at 330°C, except for the Sb layer and a thin covering layer of Si(a), which was deposited at 100°C to prevent Sb evaporation from the surface after deposition. Dense packing of silicon atoms was achieved and subsequent void formation eliminated. Laser irradiation was again performed in atmosphere and RBS results showed no detectable oxygen. Channelling results in figure 8 show that for a laser energy density of 1.50 J/cm^2, the minimum yield for the aligned crystal is 5.5%, which is indicative of excellent regrown crystal quality. (Si<100> grown with the Czochralski technique can be aligned for a minimum yield of 3%). Also, 90% of the Sb atoms were trapped in substitutional sites and are thus electrically active. The threshold for good epitaxial regrowth was found to be about 1.15 J/cm^2 for this structure, with the As doped region being buried approximately 2500 Å below the sample surface. It is interesting to note that as the laser energy is increased the epitaxial quality starts to decrease, probably owing to damage caused during laser irradiation.

17.3.5 Oxidation effects during formation of buried Sb profiles in Si<100>

R J Carolissen and R Pretorius

Amorphous silicon deposited at room temperature in an UHV system on Si<100> is known to be up to 8% less dense than silicon amorphized by ion implantation {1}. When this Si(a) is irradiated with a Q switched ruby laser, spherical voids are formed by coalescence of the free volume in the melt. These voids are stabilized in the liquid film by the presence of atmospheric gases absorbed by Si(a) when exposed to air. Prolonged melting or multiple laser irradiations cause the voids to collapse and the absorbed gases to diffuse out to the surface {1}.

Calculations based on a decrease in density of 8% show that the amount of oxygen incorporated into the deposited Si(a) could not account for the extent of oxidation observed after laser irradiation (see figure 9). It is also found that the presence of relatively high concentrations of Sb in the near surface region is necessary for this excessive oxidation to occur (see figure 10).

Evaporation of Si(a) onto a Si<100> substrate, maintained at 330°C, eliminated the free volume through denser packing of silicon atoms {2, 3}, and void formation was therefore not possible. No oxygen was detected, within the sensitivity of the RBS technique, for laser irradiated samples prepared by this method. This was true even when high concentrations of Sb were present in the near surface region.

It is clear from the above arguments that the oxygen must have been supplied from the atmosphere for such excessive oxidation to occur.

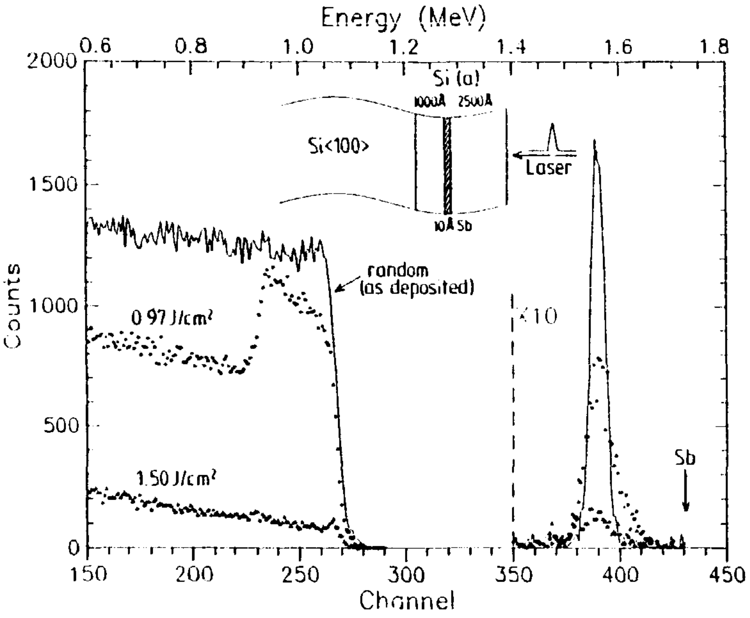

Fig. 8 Channelling measurements of a buried Sb structure formed during deposition of the Si(a) layer at a substrate temperature of 330°C and irradiated at different laser energies. It can be seen that the Sb is not at its surface position and is buried under an epitaxial regrown Si layer with a thickness of about 2600 Å. The large decrease in Sb yield at 1.50 J/cm^2 shows that most of the Sb dopant atoms occupy electrically active substitutional positions in the silicon lattice.

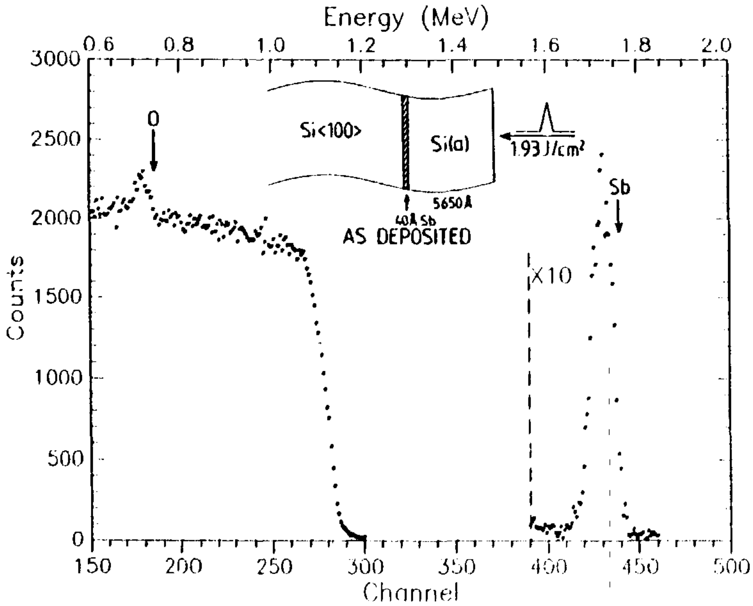

Fig. 9 RBS spectrum showing excessive oxidation (see oxygen peak) for laser annealed Si(a) which was deposited at room temperature in an UHV system.

This is only possible if the voids in the regrown region are interconnected. This is borne out by the fact that significant amounts of oxygen are detected up to depths in excess of 1000 Å (figure 10). While this region is in a molten state it is reasonable to assume that these voids or gas-filled bubbles are not connected. Upon solidification however, the strain caused by the voids can result in microcracks which connect them to each other. Therefore the major part of the oxidation must have taken place after solidification of the melt. It appears that a high concentration of Sb trapped in silicon significantly enhances the oxidation rate in an oxidising ambient.

References

1. D E Aspnes, J M Poate, G A Rozgonyi, T T Sheng, G K Celler, "Symposium on laser and electron beam processing of electronic materials", Electrochemical Society, Los Angeles (1979) (unpublished).

2. J Gonzalez-Hernandes, D Martin, S S Chao, R Tsu, Appl. Phys. Lett. 45 (1984) 101

3. S Saitoh, T Sugh, H Ishiwara and S Furukawa, Jap. J. Appl. Phys. 20 (1981) 130

17.3.6 Laser epitaxy of deposited silicon films

D Adams*, D Knoesen* and R Pretorius

* University of the Western Cape

Soon after the demonstration of the successful laser-induced epitaxy of ion-implanted single-crystal silicon in 1975, it was established that amorphous silicon layers deposited on single-crystal silicon can also be regrown epitaxially by pulsed-laser annealing.

In this investigation we have studied the deposition conditions under which good epitaxy can be achieved as well as the laser characteristics that are required. As a first step, amorphous Si layers 1000 - 4000 Å thick were deposited at room temperature by electron beam evaporation. Such amorphous silicon layers are known to be very porous, with the result that in-diffusion of atmospheric gases occurs. When melting takes place these gases are trapped inside the voids and during crystallization a bad single-crystal silicon structure is formed. To overcome this problem, we have used two approaches: (1) we deposited the amorphous Si on a substrate held at a temperature of 350°C and (2) we furnace-annealed the samples at various temperatures for 30 min after vacuum deposition of Si(a) at room temperature.

Figure 11 shows the backscattering spectra of deposited amorphous Si before and after laser irradiation. The channelled backscattering yield ($X_{min} \approx 8\%$) from the sample after laser annealing at 2.30 J/cm^2 is much lower than that from the sample before annealing, showing complete epitaxial regrowth of the amorphous silicon layer. Backscattering spectra of amorphous silicon deposited on a heated

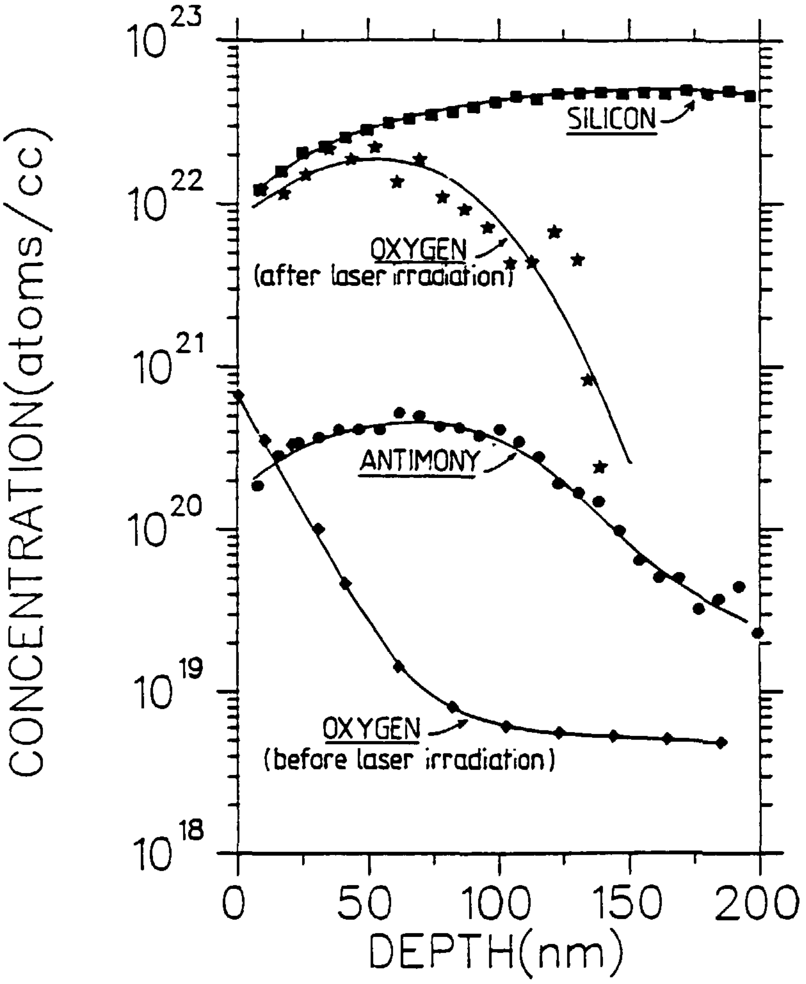

Fig. 10 Concentration profiles for a Si<100>/Sb 40 Å/Si(a) 5650 Å structure irradiated at an energy of 1.93 J/cm^2. The oxygen content of the Si(a) before laser irradiation is an extrapolation from results obtained from the literature {1}, where SIMS measurements were used on samples prepared similarly to those used in this study.

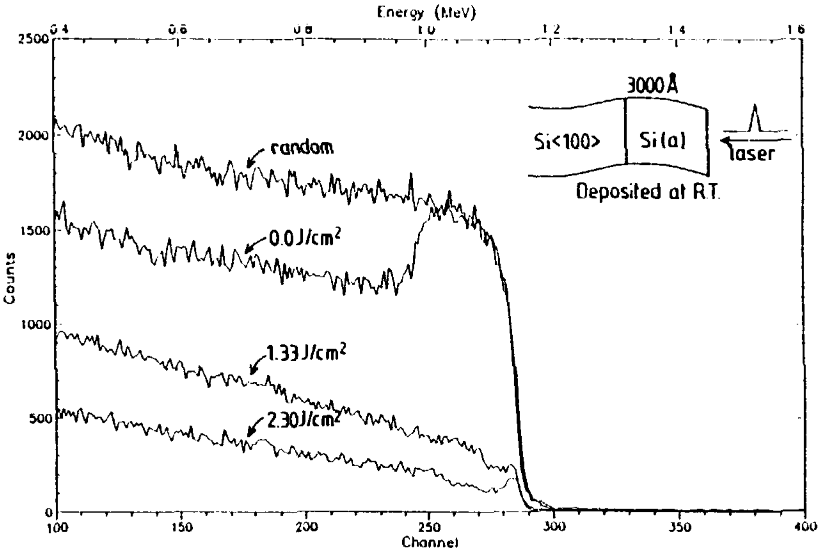

Fig. 11 RBS channelling spectra of amorphous silicon deposited at room temperature onto Si<100> substrates and irradiated at different laser energies.

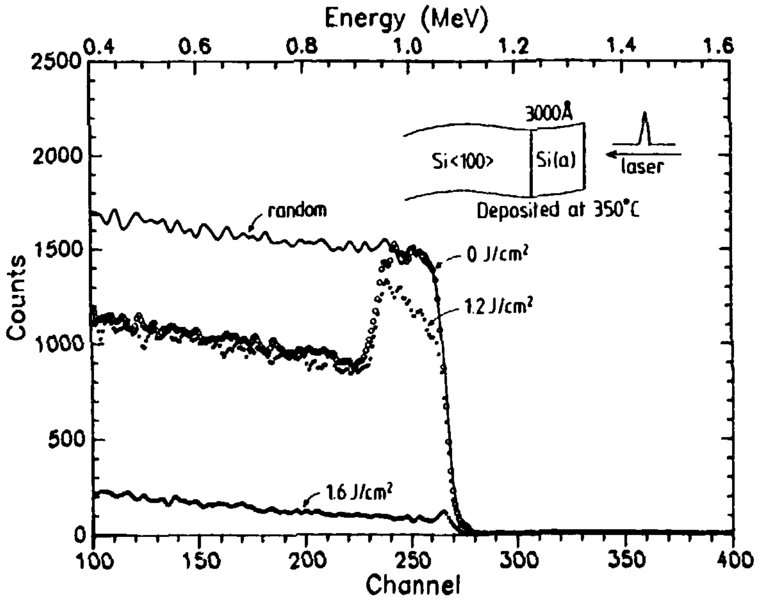

Fig. 12 RBS channelling spectra of 3000 Å of amorphous silicon deposited onto a heated (350°C) Si<100> substrate and irradiated at different laser energies. A minimum yield (channelled counts/random counts 100) of 4% at 1.6 J/cm^2 shows that excellent epitaxial regrowth has occurred.

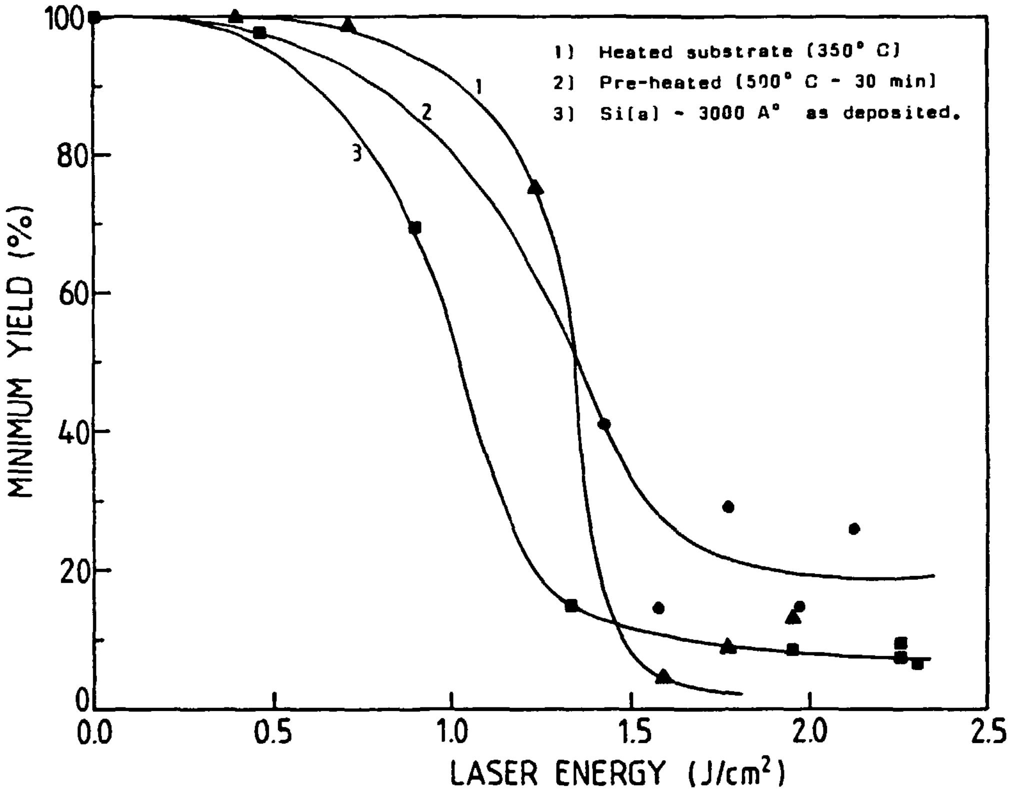

Fig. 13 The channelling minimum yield obtained as a function of laser energy for different methods of preparation of the amorphous silicon layer. It can be seen that the best results are obtained when the amorphous silicon is deposited onto a heated (350°C) substrate.

substrate (temperature ∿ 350°C) before and after laser irradiation are given in figure 12. The minimum yield of about 4% at 1.6 J/cm^2 shows excellent epitaxial regrowth of the amorphous silicon layer as the minimum yield of a perfect crystal is approximately 3%.

The minimum yield (X_{min}) as a function of laser energy for three different Si(a) layers is depicted in figure 13. Furnace preheating appears to enhance oxygen absorption resulting in very poor epitaxial regrowth, whereas the heated substrate seems to give the best results. A higher energy-density is required to induce epitaxial regrowth of the amorphous Si deposited on the heated substrate because of its lower absorption coefficient than that of the as-deposited amorphous silicon.