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DOPANT PROFILE CHANGES INDUCED BY PULSED LASER ANNEALING

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DOPANT PROFILE CHANGES INDUCED BY PULSED LASER ANNEALING*

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Changes in implanted dopant profiles as a result of pulsed laser annealing provide fundamental information on the laser annealing mechanism.[1,2] We have used secondary ion mass spectrometry (SIMS) and Rutherford ion backscattering to investigate the effects of pulsed laser annealing (Q switched ruby laser, 50 x 10^{-9} sec. pulse duration time) on silicon crystals implanted by B, P, As, Sb, Cu and Fe. Our results show that B, P, As and Sb undergo substantial redistribution in the absence of significant surface segregation during the laser annealing process. Calculations strongly suggest that the crystal can be melted to a depth of $\sim 1\mu$ and the implanted region remains in the melted state for several hundred nanoseconds. Profiles calculated for liquid phase diffusion of the dopant are shown to be in excellent agreement with the experimental results. Arsenic profiles after laser annealing are shown to be very sensitive to the laser photon energy density. Profiles for implanted Cu and Fe show significant segregation to the surface after pulsed laser annealing and this may be related to their very low segregation coefficient from the liquid.

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Single crystal silicon of (100) orientation was used for the B, P, As and Sb implants, while (111) crystals were used for the Cu and Fe implants. Implants were performed at room temperature under high vacuum conditions (2×10^{-8} Torr). Annealing was accomplished using the Q switched output of a pulsed ruby laser. Profiles for ^{11}B and ^{31}P were measured using the SIMS technique while those for ^{75}As, ^{121}Sb, ^{63}Cu and ^{56}Fe were measured using 2.5 MeV He^+ Rutherford ion backscattering in a high depth resolution scattering geometry.

Figure 1 shows experimental results for the case of ^{11}B (35 keV, $1 \times 10^{16}/cm^2$) and ^{75}As (100 keV, $1.4 \times 10^{16}/cm^2$) measured in the as-implanted and laser annealed (~ 1.5 Joules/cm^2, 60×10^{-9} sec.) conditions. Laser annealing causes a substantial redistribution of dopant both toward the surface as well as deeper into the crystal. Ion channeling measurements, transmission electron microscopy, and Hall effect measurments show these crystals to be free of any damage (down to ~ 10 Å resolution) in the form of dislocations, stacking faults or dislocation loops after laser annealing with the dopants occupying substitutional sites in the lattice. Profiles for ^{31}P and ^{121}Sb show a similar dopant redistribution as a result of pulsed laser annealing.[1]

The solid lines in Fig. 1 are profiles calculated for liquid phase diffusion of the dopants from the as-implanted profile. Previous calculations[2] have shown that under the conditions used in these laser annealing experiments (1.5 Joules/cm^2, 60×10^{-9} sec. pulse duration time) the as-implanted crystal can be melted to a depth of $\sim 1\mu m$ by the incident laser light. Results of these calculations[2] are summarized in Fig. 2 which shows the temperature profile in the sample at the termination of the laser pulse (Fig. 2a) and the calculated melt front position as a function of time, Fig. 2b. The lower curve of Fig. 2a is a computer solution to the one dimensional heat conduction equation allowing for the possibility of a phase change (melting) and non-linearities in thermal conductivity and specific heat. Details of these calculations are in Ref. (2).

The calculated melt front position is shown in Fig. 2b as a function of time. Penetration of the melted region to a depth of almost of 1μm is predicted and the average velocity of the melt front as it receeds back toward the surface is ∿ 270 cm/sec. While this occurs, a region that is several thousand angstroms deep remains melted for time periods of several hundred nanoseconds. During this time the as-implanted dopants can diffuse in the liquid where diffusion coefficients are much higher than in the solid.

In Fig. 1, there is excellent agreement between the experimental profiles measured after laser annealing and the calculated profiles which are single parameter fits of the quantity $D\tau$ to the solution of the standard mass diffusion equation. From the calculated profiles the quantity $D\tau$ is obtained and using literature values[3] for diffusion coefficients in <u>liquid</u> silicon, a value for the diffusion time ($\tau_{B \text{ in } Si} = 180 \times 10^{-9}$, $\tau_{As \text{ in } Si} = 270 \times 10^{-9}$) can be extracted. These are in reasonable agreement with predictions of the melt front position (Fig. 2b). Equally good fits to P and Sb profiles have also been obtained with diffusion times being in the same range. The pulsed laser annealing process is therefore viewed as one in which the incident laser light melts the crystal to a depth of several thousand angstroms. The melted region recrystallizes epitaxially from the underlying substrate by means of liquid phase epitaxial regrowth. Long range dopant diffusion takes place during the time the implanted region is in the liquid state. Similar conclusions regarding melting during pulsed laser annealing have been reported by others.[4,5]

Figure 3 illustrates how profiles for arsenic change as a function of laser energy density in the range of 0.6 to 1.4 Joules/cm^2. At the lowest laser energy density (0.63 Joules/cm^2) there is redistribution of the dopant only in the region extending from the surface down to a depth of ~950 Å, indicating that the melt front penetrated to at least 950 Å at this energy density. Transmission electron microscopy shows the structure to be polycrystalline in this depth interval,[6] indicating that regrowth is not epitaxial presumable because the melt front did not penetrate through the initial amorphous layer to the underlying substrate. At 1.07 Joules/cm^2, spreading of the profile toward the surface and deeper into the crystal is observed. Defect-free single crystal structure with the same orientation as the underlying substrate is observed by TEM[6] indicating epitaxial regrowth. There is, however, a thin layer ~200 Å thick containing residual damage on the surface of this crystal. At 1.41 Joules/cm^2 the profile is nearly uniform in the surface region. Comparison of these profiles to calculations requires that the time evolution of the melt front position be explicitly incorporated into the mass diffusion equation. Such calculations are being carried out now and will be the subject of a separate publication.

The profiles of B, P, As and Sb after laser annealing show redistribution of the dopant in the absence of any significant surface segregation. This, however, is not the case for impurities such as Cu and Fe. Figure 4 shows profiles for Cu in <111> silicon in the as-implanted and laser annealed conditions. Laser annealing (~1.4 J/cm^2) results in almost complete segregation of copper to the surface with no loss of the implanted impurity.

The behavior of copper is believed to be related to the very low value of the distribution coefficient from the melt ($k = C_S/C_L$) and its low solid solubility limit. For Cu the equilibrium distribution coefficient[7] is ~4 x 10^{-4}. This implies that Cu will be rejected to the liquid as the melt front moves toward the surface, thus enhancing the Cu concentration in the liquid over a limited region at the solid-liquid interface. The effective distribution coefficient[8] may be significantly higher than the equilibrium value, however, because the melt front velocity is larger than the diffusion rate in the liquid if we assume typical liquid phase diffusion coefficients $D \sim 10^{-4}$ cm^2/sec. Complete segregation to the near-surface region as is the case for Cu, appears to be possible only if the rejected impurity diffuses away from the liquid solid interface at a rate comparable to the melt front motion or if the distribution coefficient depends on the concentration at the interface. Model calculations are being carried out which will attempt to include the effects of the distribution coefficients on the profile.

Preliminary results for ^{56}Fe implanted silicon indicate that Fe also segregates toward the surface, but not to the same extent as copper. The behavior for Fe is currently under further investigation.

In conclusion, our results show that dopants such as B, P, As and Sb undergo substantial long-range motion during pulsed laser annealing. Dopant profiles are shown to be consistent with the picture that the laser light melts the crystal to a depth of several thousand angstroms and that recrystallization takes place by means of liquid phase epitaxial regrowth resulting in defect-free single crystal material with dopants in substitutional lattice sites. Redistribution of dopants takes place by normal diffusion in the liquid state over time periods of 200-300 x 10^{-9} sec. At low energy densities (0.63 Joules/cm^2) dopant diffusion takes place over a limited depth interval ($\sim$950 Å) and the resulting crystal structure is polycrystalline rather than single crystal. Copper (and iron) both show masssive segregation to the surface after pulsed laser annealing. This is believed to be related to the very low segregation coefficients from the melt and the very low limits of solid solubility, but model calculations are necessary to understand this phenomena in detail.

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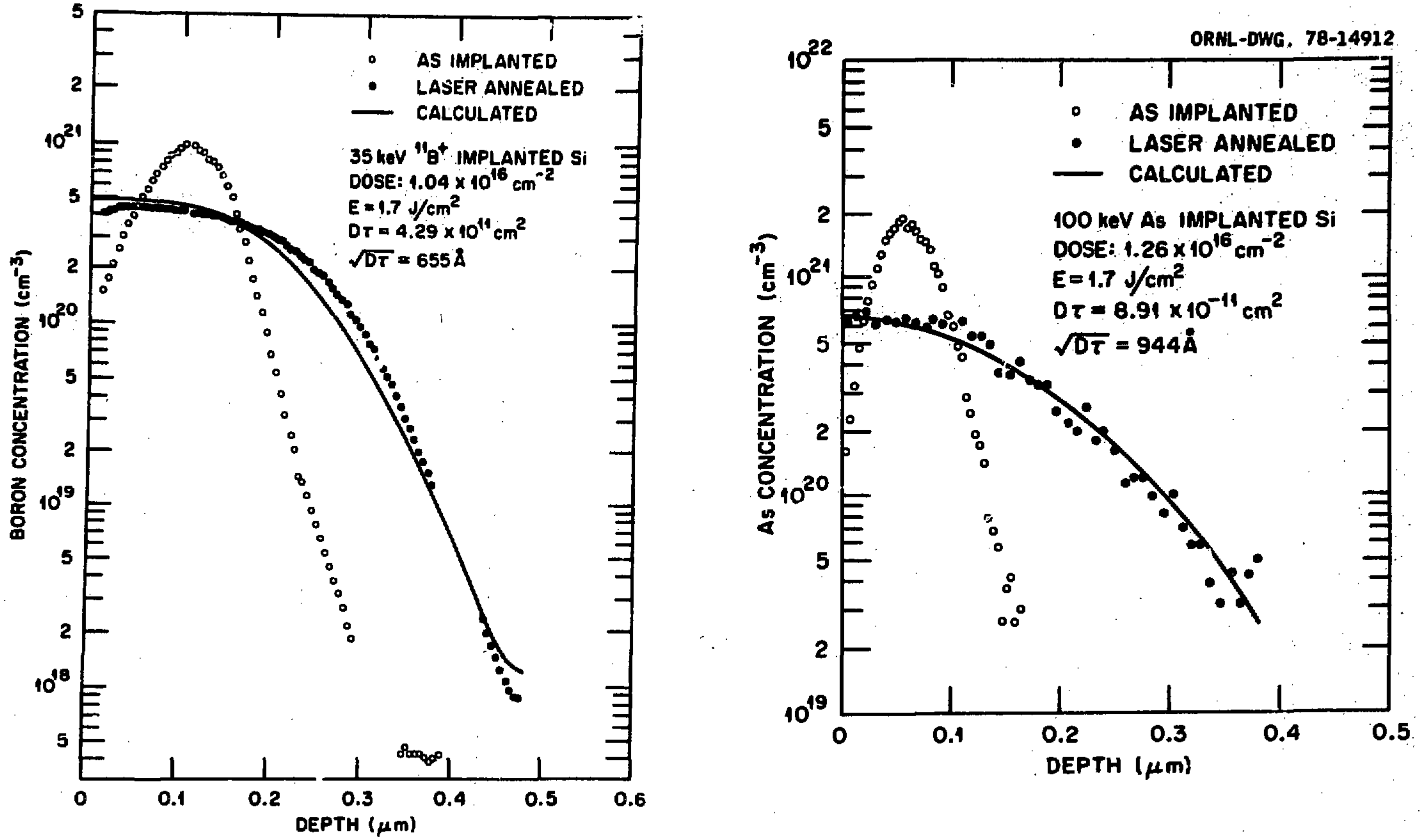
AS IMPLANTED
LASER ANNEALED
CALCULATED
35 keV $^{11}B^+$ IMPLANTED Si
DOSE: 1.04×10^{16} cm^{-2}
E = 1.7 J/cm^2
$D\tau = 4.29 \times 10^{11}$ cm^2
$\sqrt{D\tau}$ = 655 Å
BORON CONCENTRATION (cm^{-3})
10^{21}
10^{20}
10^{19}
10^{18}
5
2
DEPTH (μm)
0
0.1
0.2
0.3
0.4
0.5
0.6
ORNL-DWG. 78-14912
AS IMPLANTED
LASER ANNEALED
CALCULATED
100 keV As IMPLANTED Si
DOSE: 1.26×10^{16} cm^{-2}
E = 1.7 J/cm^2
$D\tau = 8.91 \times 10^{-11}$ cm^2
$\sqrt{D\tau}$ = 944 Å
As CONCENTRATION (cm^{-3})
10^{22}
10^{21}
10^{20}
10^{19}
5
2
DEPTH (μm)
0
0.1
0.2
0.3
0.4
0.5

Fig. 1

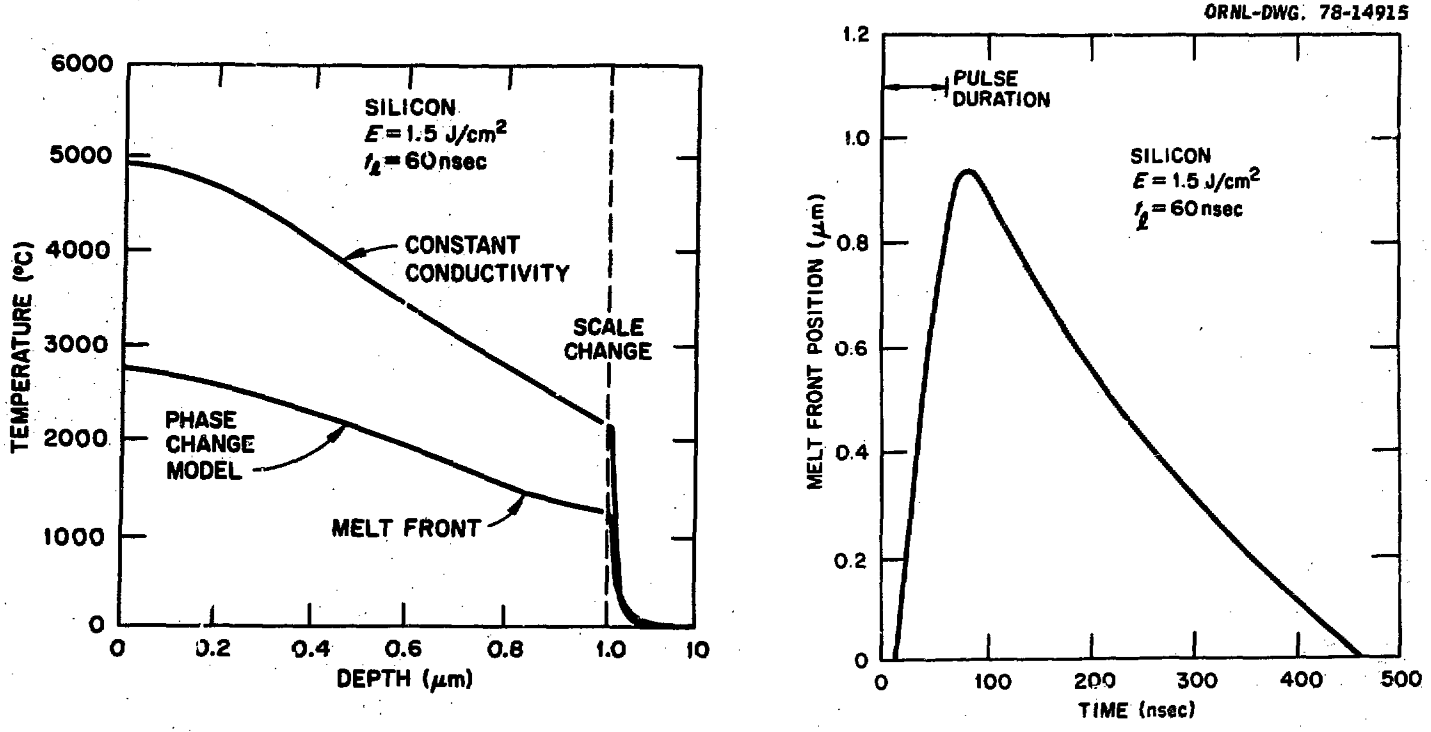
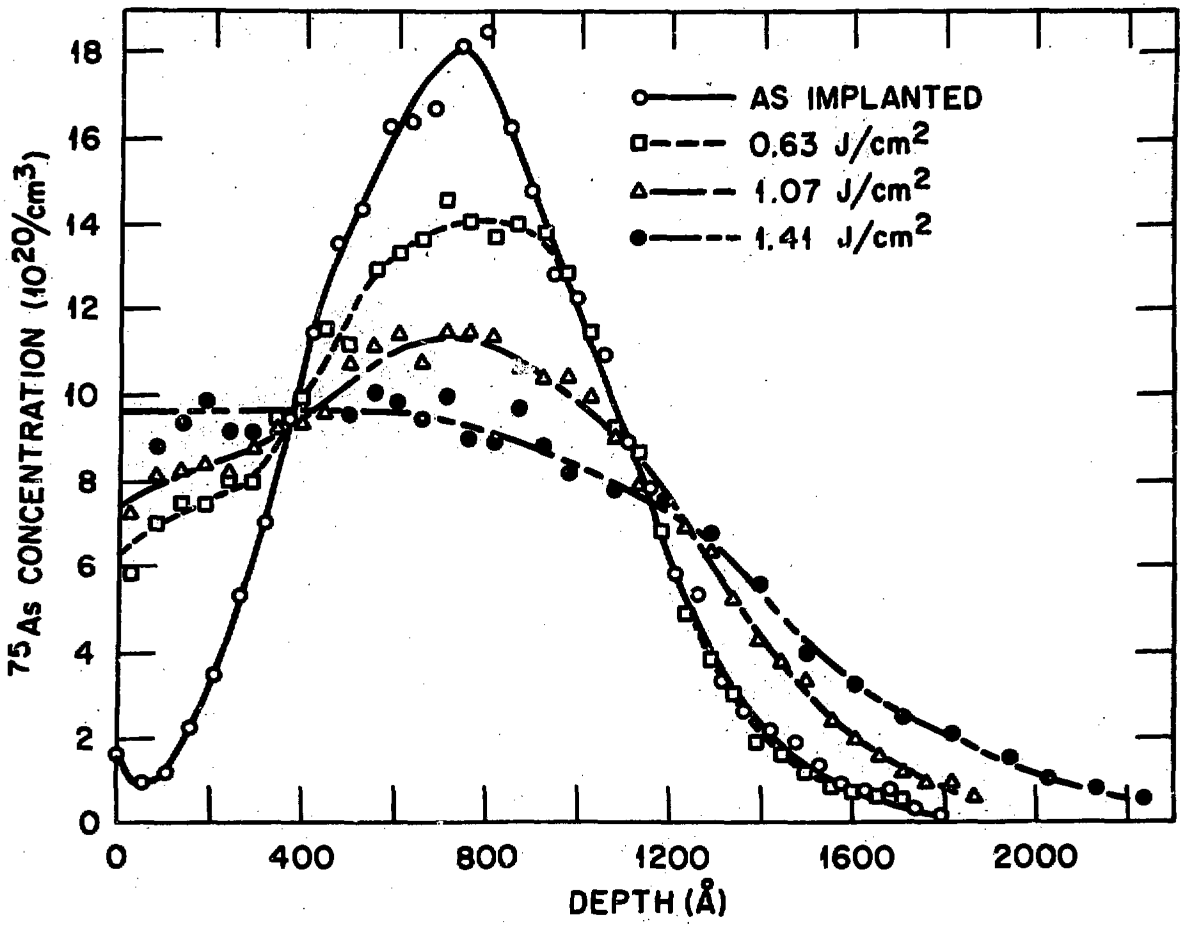
ORNL-DWG. 78-14915
6000
5000
4000
3000
2000
1000
0
TEMPERATURE (°C)
SILICON
E = 1.5 J/cm²
t_ℓ = 60 nsec
CONSTANT CONDUCTIVITY
SCALE CHANGE
PHASE CHANGE MODEL
MELT FRONT
0
0.2
0.4
0.6
0.8
1.0
10
DEPTH (μm)
1.2
1.0
0.8
0.6
0.4
0.2
0
MELT FRONT POSITION (μm)
PULSE DURATION
SILICON
E = 1.5 J/cm²
t_ℓ = 60 nsec
0
100
200
300
400
500
TIME (nsec)

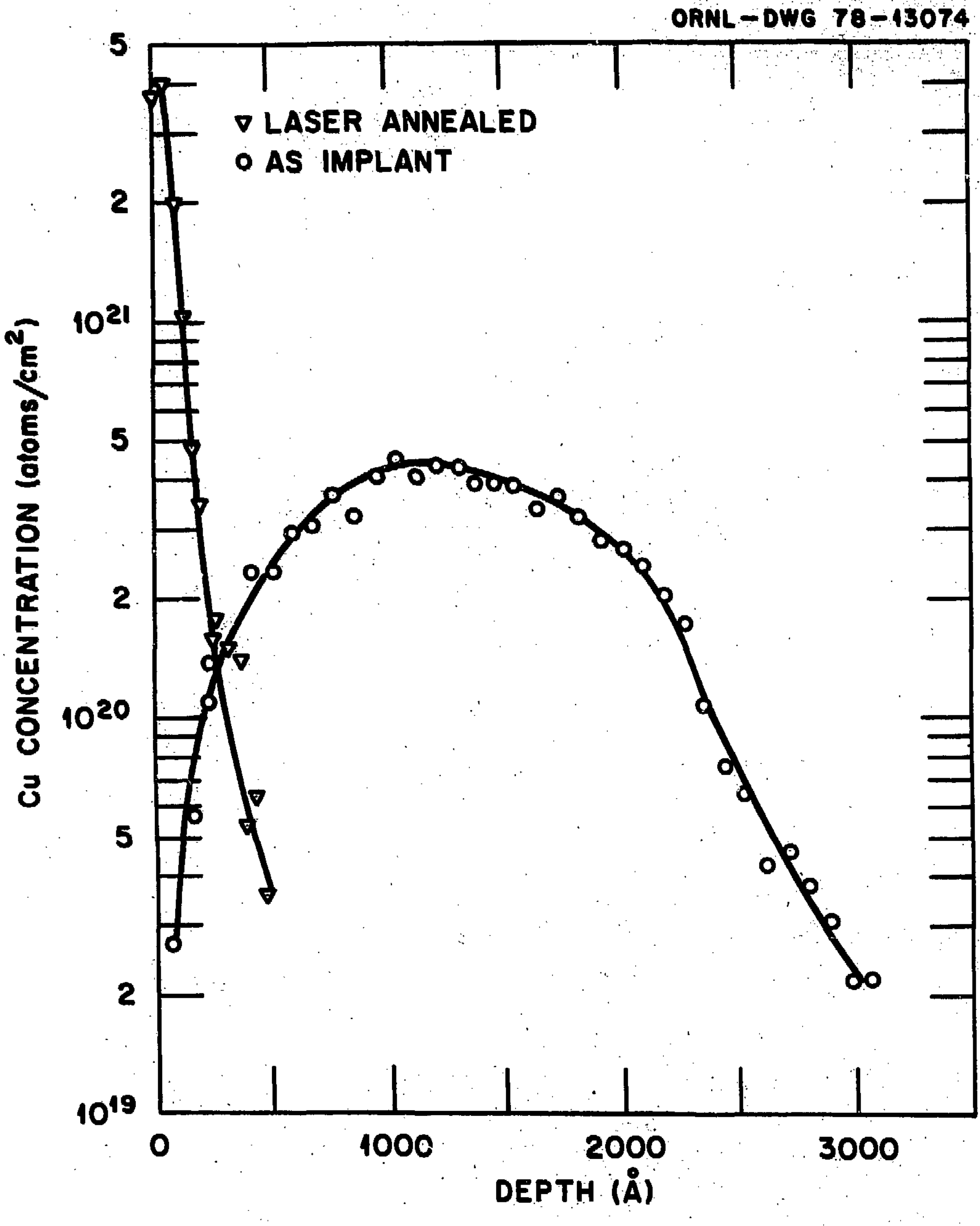
Fig. 2

ORNL-DWG 78-13372



^{75}As (100 keV, 1.4×10^{16}/cm^2) IN ⟨100⟩ Si

Fig. 3



$^{63}Cu^+$ (150 keV, $6.9 \times 10^{15}/cm^2$) in ⟨111⟩ Si

Fig. 4