$=0.534-0.55$. Using η_a and liquid-state perturbation theory, we may generate the phase boundary in the entire (P^*, T^*) plane for the Lennard-Jones 12-6 fluid *or another chosen fluid described by a different interatomic potential.*

One of us (H.R.W.) thanks N.-H. Tsai for help with the programming involved.

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Segregation Effects in Cu-Implanted Si after Laser-Pulse Melting

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Cu-implanted Si crystals were irradiated with Q-switched ruby-laser single pulses. After irradiation with energy density in excess of 1.0 J/cm^2, the Cu atoms accumulate at the sample surface. Thermal annealing in the 500–800°C range casues a migration of Cu inside the specimen, in agreement with diffusion coefficient and solid solubility values. The results indicate the formation of a liquid layer induced by laser irradiation. The solid-liquid interface movement during freezing qualitatively justifies the observed surface accumulation.

High-power laser pulses were used recently to anneal out the damage in ion-implanted semiconductors.[1-6] The transition of an amorphous layer to a single-crystal structure was ascribed to the laser-induced melting of the surface layer.[7,8] Liquid phase epitaxial growth on the underlying single-crystal substrate occurs during the subsequent freezing. Changes in the ion-implanted profiles were also accounted for by a liquid formation.[7] The time involved in the Q-switched laser irradiation ($\sim 10^{-7}$–10^{-8} s) cannot in fact allow detectable atom migration in the solid phase with the usual activation energies.

These effects could be also interpreted in terms of ionization-enhanced diffusion.[9] The high density of absorbed photons with energy greater than the band gap produces a large amount of broken bonds between nearest-neighbor atoms or nonequilibrium hole-electron pairs which can enhance the mobility of a defect. The observed growth rates and impurity diffusion coefficients could be then described in terms of kinetic processes in a solid medium with suitable low values of the activation energies, without invoking any liquid formation.

In the present work we show that Q-switched ruby laser pulses with power densities higher than 20 MW/cm^2 and 50-ns duration induce liquid formation in ion-implanted Si.

Silicon single crystals, 300 μm thick and $\langle 100 \rangle$ oriented, were implanted at room temperature with 70-keV Cu^+ to a fluence 2×10^{15} ions/cm^2. After implantation some samples were irradiated with pulsing ruby laser ($\lambda = = 0.694$ μm) in the energy density range between 1.0 and 3.0 J/cm^2. Other samples were thermally annealed, under vacuum condition ($\sim 10^{-5}$ Torr), in the temperature range 500–850°C for isochronal steps of 30 min. MeV He particles scattered at 102° away from the beam incidence were used to analyze in depth the Cu distribution. The energy-to-depth conversion was obtained using stopping cross sec-

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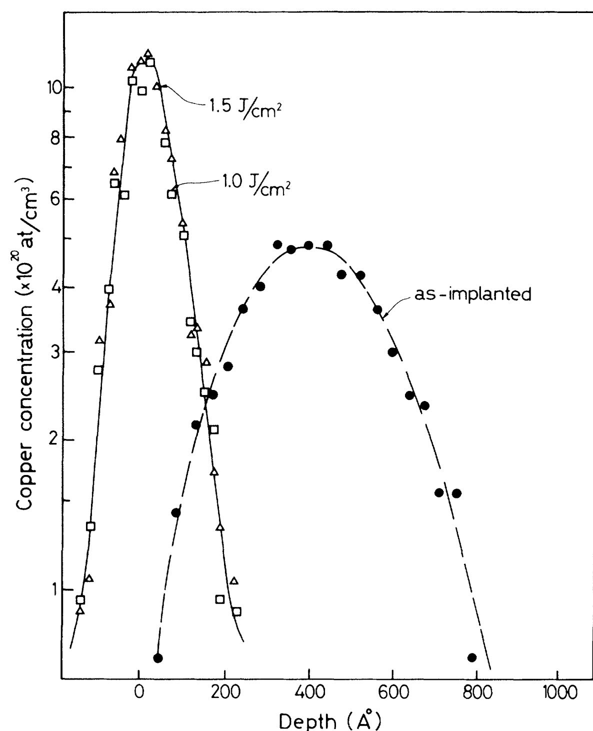

FIG. 1. Cu concentration profiles in Cu-implanted Si samples after pulsing ruby laser irradiation of 1.0 and 1.5 J/cm^2. The as-implanted profile is reported for comparison.

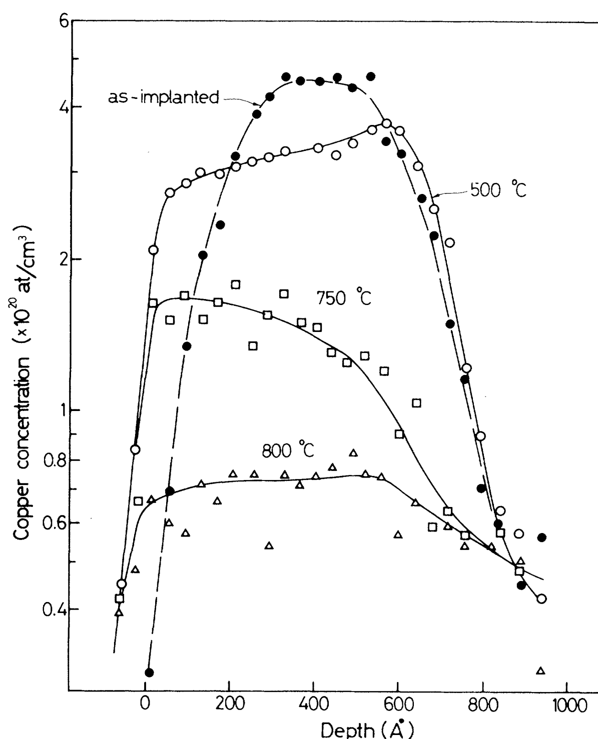

FIG. 2. Cu concentration profiles in Cu-implanted Si samples after 30 min annealing at 500, 750, and 800°C.

tions tabulated by Ziegler and Chu.[10] The experimental conditions led to a depth resolution of about 100 Å. The Cu projected range R_p and standard deviation ΔR_p are 480 and 175 Å, respectively.[11]

The Cu concentration profiles are shown in Figs. 1 and 2 after laser and thermal annealing, respectively. For comparison the as-implanted profile is also reported. The yields indicate that after laser irradiation with energy densities exceeding 1.0 J/cm^2 all the implanted Cu atoms accumulated at the sample surface.

A different behavior is observed after thermal annealing. At 500°C for 30 min, the Cu profile becomes flat within a depth of about 700 Å. At annealing temperatures higher than 700°C a noticeable reduction in the yield is observed. The Cu diffusion coefficient in Si is of the order of 10^{-4}–10^{-5} cm^2/s in the temperature range 500–800°C.[12] Diffusion of Cu atoms through the 300-μm-thick Si sample occurs then during the 30-min annealing. The solid solubility of Cu in Si is[13] 10^{15} cm^{-3} at 500°C, 10^{16} cm^{-3} at 700°C, and 5×10^{16} cm^{-3} at 800°C. If the copper concentration reaches the solid solubility in the overall crystal, at 700°C only 15% of the implanted Cu is allowed to be distributed into the bulk, about 50% at 760°C, and 75% at 800°C. These simple estimates are in good agreement with the measured amount of Cu remaining in the implanted region as reported in Fig. 2.

Similar profiles should be obtained after laser irradiation if the Cu migration were to occur in a heavily ionized solid medium with a large diffusion rate. Laser irradiation causes instead a strong accumulation of Cu at the sample surface (see Fig. 1) which can be explained by including a melting process. Calculations were performed with the assumption that all the absorbed light energy is instantaneously converted into heat.[7,14] The heat equation was solved numerically including the structure dependence of the light absorption coefficient and accounting for the temperature dependence of thermal conductivity. The results of the calculations indicate that an energy density of the pulse in excess of a threshold value is required to melt the silicon surface and the thickness of the melted layer increases with the energy density. The melting proceeds by a solid-liquid interface movement toward the interior of

the sample for a time interval comparable to the pulse duration (50 ns). The freezing starts at the end of the pulse and the solid-liquid interface moves back to the sample surface.

The freezing rate and the ratio between the impurity equilibrium solubilities in the solid and liquid phases determine the final dopant profile. The equilibrium segregation coefficient, k_0, of Cu in Si (Ref. 15) is 4×10^{-4} so that it accumulates in the liquid phase. The described kinetics of the solid-liquid interface then justifies the surface accumulation of Cu after laser irradiation.

The interface velocity during the freezing process is determined by the rate of dissipation of the latent heat and then by the temperature gradient along the sample. By the previous calculations[7] we get an average temperature gradient of about 10^6 K/cm in the proximity of the solid-liquid interface. This value led to a freezing rate of about 200 cm/s, which is at least four orders of magnitude larger than those of crystal growth from the melt or zone refining.[16]

The effective distribution coefficient approaches 1 with increasing growth rate if the melt is large enough. In our case the existing treatments of segregation cannot be applied because the thickness of the transient region exceeds the total melted length by less than 1 μm. We calculated the final profile according to the following assumptions: The liquid was divided into steps of thickness Δx_i, solidification of the first layer occurs in time interval $\Delta t = \Delta x/V$; the advancing solid-liquid interface rejects in the nearest liquid layer, Δx_{i-1}, the impurity amount $c_L(x_i)(1-k_0)\,\Delta x_i$ per unit area, c_L being the impurity concentration in the liquid phase. These impurities are allowed to migrate with a diffusion coefficient $D_L = 10^{-4}$ cm^2/s in the remaining liquid region for a time interval Δt. The boundary condition is $c_L = \mathrm{cos}t$ at $t=0$. The thickness Δx used in the calculations was smaller than $2D_L/V$, i.e., 100 Å, and the diffusion equation was solved for time intervals much less than Δt. This approach is similar to that of Tiller *et al.*[17] and the results are summarized in Fig. 3 where the fraction of impurities accumulated in the last 10% of the initial liquid-layer thickness is plotted as a function of the equilibrium distribution coefficient k_0. The results are shown for 2000 Å and 20 μm, together with the curve corresponding to a negligible interface velocity. In the 2000-Å-thick liquid layer the amount of Cu segregated in the last 200-Å surface region reaches the 90% for k_0 values of 10^{-2} while in the 20-μm layer the corresponding

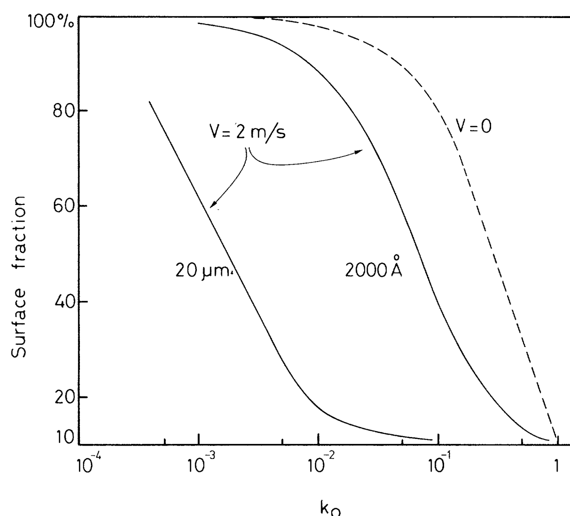

FIG. 3. Calculated amount of Cu accumulated at the surface (10% of the total liquid thickness) vs the equilibrium distribution coefficient k_0 for two liquid layer thickness, 2000 Å and 20 μm, and for a freezing rate of 2 m/s. The curve calculated for a negligible interface speed is also shown (dashed line).

amount in the last 2000 Å is less than 20%. These calculations justify the strong segregation effects detected for Cu where k_0 is 4×10^{-4}.

In conclusion, laser irradiation of Cu-implanted Si at energy densities larger than 1.0 J/cm^2 causes a melting of the surface layer with a consequent accumulation of Cu atoms at the crystal surface during the solidification. The effect is related to the low value of the segregation coefficient. Moreover the high growth rate, several orders of magnitude higher than the normal values, allows segregation only for impurities distributed in liquid layers a few thousand angstroms thick, as shown by calculations. Thermal annealing causes instead a very fast diffusion of Cu all over the Si sample.

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Inter-Valence-Band Absorption in Electron-Hole Droplets

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The broad line shape for absorption due to transitions between heavy-hole and spin-orbit bands in electron-hole droplets in Ge is explained. The calculation uses multiple-scattering concepts to remove the divergences of ordinary perturbation expansions in the dynamical Coulomb interaction. The absorption resembles the free-hole theory at low frequencies, is sensitive to both band anisotropy and screening approximations at intermediate frequencies, and is independent of screening at high frequencies.

Free-particle theories of line shapes assume that electrons and holes occupy single momentum states inside renormalized conduction and valence bands. This idea has successfully explained the luminescence line shape of electron-hole droplets in indirect-band-gap semiconductors where phonons take away the momentum difference between initial and final states.[1] For direct transitions the spectra are expected to show sharp structure because momentum must be conserved. Therefore, any physical effects which change particle momentum will more profoundly affect line shapes for direct transitions. Fits to transitions between heavy-hole and light-hole bands responsible for the plasmon width in electron-hole droplets (EHD) require broadening parameters of several meV.[2] The gain spectra of highly excited direct-band-gap semiconductors are better fitted by an assumption of no-momentum conservation.[3] Thus, free-particle theories are less successful for direct transitions.

In this Letter, we discuss the observation by Pokrovsky and Svistunova.[4] that absorption due to transitions between the heavy- and light-hole bands and the spin-orbit-split band in Ge is much broader than predicted by free-particle theory (Fig. 1). One approach to this problem would be to follow Landsberg[5] in broadening the initial and final states with their random-phase-approximation (RPA) widths. However, this would predict a slowly decreasing cross section below the free-particle threshold in qualitative disagreement with experiment. A second approach would be to calculate the correction to the free-particle theory to first order in a dynamically screened Coulomb interaction. The calculation might include the same diagrams which Brinkman and Lee[6] applied to the gain spectra of direct-gap semiconductors. Unfortunately, this leads to divergent answers for our problem because it is kinematically possible for the intermediate states to be on the energy shell.

We present the first explanation of inter-valence-band transitions in EHD and in degenerately doped p-type Ge. The absorption is calculated including the physical processes which create single plasmon or particle-hole pairs. An approximation motivated by multiple-scattering theory is introduced which removes the divergences of ordinary perturbation expansions. The

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