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FORMATION OF SUPERSATURATED ALLOYS BY PULSED LASER ANNEALING

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KINETIC EFFECTS AND MECHANISMS LIMITING SUBSTITUTIONAL SOLUBILITY IN THE FORMATION OF SUPERSATURATED ALLOYS BY PULSED LASER ANNEALING*

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ABSTRACT

Pulsed laser annealing of silicon implanted by Group (III,V) dopants leads to the formation of supersaturated alloys by nonequilibrium processes occurring in the interfacial region during liquid phase epitaxial regrowth. The distribution coefficient from the melt (k') and the maximum dopant substitutional solubility ($C_s^{\max}$) are far greater than equilibrium values and both are functions of growth velocity. Substitutional solubility is limited by lattice strain and by constitutional supercooling at the interface during regrowth. Values for $C_s^{\max}$ obtained at different growth velocities are compared with predictions of thermodynamic limits for solute trapping.

INTRODUCTION

Extensive investigations [1-4] have shown that pulsed laser annealing can be used to process ion implanted semiconductors in order to achieve materials properties which cannot be obtained by conventional methods. These investigations have demonstrated that Group (III,V) dopants can be incorporated into substitutional lattice sites in silicon at concentrations that far exceed equilibrium solubility limits [5,6]. In pulsed laser annealing, experimental [7] and theoretical studies [8,9] provide strong evidence that the adsorbed laser radiation leads to melting of the near surface region followed by liquid phase epitaxial regrowth from the underlying substrate at velocities calculated to be several meters/sec. Recrystallization of the melted region takes place under conditions that are far from equilibrium at the interface. Values for the interfacial distribution coefficient from the melt (k') can be determined by comparing model calculations to measurements of dopant concentration profiles after annealing [6] (k' is defined as $k' = C_s/C_L$ where C_s and C_L are the dopant concentrations in solution in the solid and liquid phase at the interface). Values for k' significantly exceed equilibrium values. For each dopant there is a maximum concentration ($C_s^{\max}$) which can be incorporated substitutionally into the lattice during laser annealing [6]. Measured values for $C_s^{\max}$ greatly exceed equilibrium solubility limits.

In this paper we discuss the formation of supersaturated solid solutions in silicon during pulsed laser annealing. We show that both k' and $C_s^{\max}$ are functions of growth velocity. We discuss the mechanisms limiting the substitutional solubilities which can be achieved by laser annealing, and we compare results for $C_s^{\max}$ obtained at two different growth velocities with theoretical predictions [10] of thermodynamic limits for solute solubility in silicon at infinite growth velocity.

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DETAILS OF EXPERIMENTAL MEASUREMENTS

Group (III,V) dopants (B, Ga, In, As, Sb, Bi) were implanted into (100) silicon single crystals at energies in the range 35 keV to 250 keV and at doses in the range 10^{15} to $10^{17}/\text{cm}^2$. Annealing was accomplished using the Q-switched output of a pulsed ruby laser at energy densities in the range $1\text{--}2 \text{ J}/\text{cm}^2$ (15×10^{-9} sec pulse duration time). These conditions result in a liquid phase epitaxial regrowth velocity of ~ 4.5 meters/sec. To change the velocity of regrowth, crystals were annealed with the substrate at temperatures in the range 650 K to 4 K. In this manner, regrowth velocity could be varied in the range ~ 1.5 m/sec to ~ 6 m/sec. Crystals were examined using 2.5 MeV He^+ Rutherford backscattering and ion channeling techniques. For low dose implants, profiles after laser annealing were compared to calculations using a model which incorporates liquid phase diffusion and a distribution coefficient from the liquid (k') during regrowth. Details are given in Ref. 6. From this comparison, values for k' were determined. For crystals implanted to high doses ($> 1 \times 10^{16}/\text{cm}^2$) backscattering and channeling measurements were used to compare the total dopant concentration and the substitutional dopant concentration, as a function of depth. Values for $C_{\text{S}}^{\text{max}}$ were determined from this comparison.

EXPERIMENTAL RESULTS

Distribution Coefficients and the Formation of Supersaturated Alloys

Figure 1 shows results for the case of Bi in Si. Laser annealing causes $\sim 15\%$ of the Bi to be segregated to the surface, but Bi remaining in the bulk of the crystal is $> 95\%$ substitutional even though the concentration exceeds the equilibrium solubility limit by factors of up to 500. This demonstrates the formation of a supersaturated alloy during laser annealing. The solid line in Fig. 1 is a calculated profile using a value of 0.4 for the distribution coefficient. By contrast, the equilibrium distribution coefficient (k_0) [11] is 7×10^{-4} , and if regrowth occurred under conditions of local equilibrium at the interface, the dotted line would be the expected profile in the bulk and essentially all of the Bi would be segregated to the surface. Clearly this does not fit the data. The departure from local equilibrium is brought about by the high velocity of the liquid-solid interface during regrowth (~ 4.5 m/sec).

Values for k' have been determined for four other dopants in silicon [6] during laser annealing. These results are summarized in Table I and compared to equilibrium values k_0 . In each case, the high velocity of regrowth causes a substantial increase in the distribution coefficient relative to the equilibrium value. Results presented in Table I were the first measurements of distribution coefficients under conditions of nonequilibrium crystal growth for any system.

Values for the distribution coefficient during regrowth should be a function of growth velocity and Fig. 2 shows that this is the case. Laser annealing at substrate temperatures of 650 K, 300 K, and 100 K gives rise to regrowth velocities of ~ 1.5 , 4.5 and 6.0 m/sec. Figure 2 shows that at low regrowth velocities a large fraction of the implanted Bi ($\sim 55\%$) is segregated to the surface and the value for k' is ~ 0.1 . At high regrowth velocity only $\sim 5\%$ of the Bi is segregated to the surface and the value for k' is ~ 0.45 . (The small discrepancy between k' values in Fig. 1 and the 300 K results of Fig. 2 is related to the accuracy with which k' can be determined.)

Maximum Substitutional Solubilities

For each dopant there is a maximum concentration ($C_{\text{S}}^{\text{max}}$) which can be incorporated substitutionally into the lattice [6]. This is demonstrated in the profiles of Fig. 3 for the case of In implanted Si. The In is highly substitutional in the lattice, up to a concentration of $\sim 1.5 \times 10^{20}/\text{cm}^3$, but in the near surface region, where the total dopant concentration rises above $10^{21}/\text{cm}^3$, the

Fig. 1. Profiles for ^{209}Bi (250 keV, $5.9 \times 10^{15}/\text{cm}^2$) in (100) Si compared to model calculations.

substitutional concentration remains relatively constant. Therefore the maximum substitutional solubility (C_s^{max}) for In in Si under these annealing conditions is $1.5 \times 10^{20}/\text{cm}^3$.

Values for C_s^{max} have been determined for five dopants in silicon [6] at a growth velocity of ~ 4.5 m/sec. These values are listed in Table II [under the

TABLE I

Distribution coefficients (k') obtained during laser annealing compared to equilibrium distribution coefficients (k_0). Regrowth velocity is ~ 4.5 m/sec except for Sb where the velocity is ~ 2.7 m/sec.

Dopant	k_0	k'
As	0.3	1.0
Sb	0.023	0.7
Bi	0.0007	0.4
Ga	0.008	0.2
In	0.0004	0.15

Fig. 2. Pulsed laser annealing of ^{209}Bi (250 keV, $1.1 \times 10^{15}/\text{cm}^2$) at different substrate temperatures.

column labeled C_S^{max} (300 K)] and compared to equilibrium solubility limits (C_S^0). (For Sb the growth velocity is ~ 2.7 m/sec.) In Table II, values for C_S^{max} (300 K) exceed those for (C_S^0) by factors that range from 4 to As to ~ 500 for Bi. Each of these alloy systems exhibits retrograde solubility in that on the equilibrium phase diagram (see Fig. 5) the dopant has its maximum concentration at a temperature that is not related to a eutectic temperature. The retrograde maximum concentration cannot be exceeded by solidification from the liquid unless there is a departure from local equilibrium at the interface during regrowth [12]. The large values for C_S^{max} (300 K) relative to C_S^0 convincingly demonstrate the nonequilibrium nature of the laser annealing induced liquid phase epitaxial regrowth process. Dopant incorporation into the lattice during this high speed growth process is by means of "solute trapping" [9,10,12,13].

TABLE II

Maximum substitutional dopant concentration in silicon (C_S^{max}) after laser annealing at substrate temperatures of 300 K and 77 K, compared to equilibrium solubility limits (C_S^0) and predicted thermodynamic limits to solute trapping (C_S^L).

Dopant	C_S^0 (cm^{-3})	C_S^{max} (300 K) (cm^{-3})	C_S^{max} (77K) (cm^{-3})	C_S^L (cm^{-3})
As	1.5×10^{21}	6.0×10^{21}	6.0×10^{21}	5×10^{21}
Sb	7.0×10^{19}	1.3×10^{21}	---	3×10^{21}
Ga	4.5×10^{20}	4.5×10^{20}	8.8×10^{20}	6×10^{21}
In	8.0×10^{17}	1.5×10^{20}	2.8×10^{20}	2×10^{21}
Bi	8.0×10^{17}	4.0×10^{20}	1.1×10^{21}	1×10^{21}

CONCENTRATION PROFILE

MICROSTRUCTURE

Fig. 3. Profiles (left) and microstructure (right) for ¹¹⁵In (125 keV, $1.3 \times 10^{16}/\text{cm}^2$) in (100) Si after laser annealing.

MECHANISMS LIMITING SUBSTITUTIONAL SOLUBILITY

Substitutional solubilities achieved by pulsed laser annealing of silicon implanted by Group (III,V) dopants are limited by three mechanisms. The first of these, which dominates for the case of B in Si, is lattice strain [14]. When B is incorporated substitutionally into the silicon lattice during laser annealing, the lattice undergoes a one dimensional contraction in the implanted region [15]. Lattice contraction gives rise to strain in the implanted region, and the magnitude is proportional to the local B concentration. When the strain exceeds the fracture strength of Si, cracks develop in the implanted region. This occurs at a B concentration of ~4 atomic % in (100) Si and is clearly shown by the SEM micrographs of Fig. 4. After laser annealing, cracks (~1 μ wide) are observed in the implanted region. These cracks penetrate to a depth of ~1 μ and run the entire length of the sample (~1 cm). To reduce lattice strain and incorporate more B substitutionally, it would be necessary to simultaneously incorporate a dopant which gives rise to a lattice expansion. Possible candidates are Ga, In or Bi.

The second mechanism which limits substitutional solubility during laser annealing is the interfacial instability which develops during regrowth and leads to lateral segregation of the rejected dopant and the formation of a well defined cell structure in the implanted region [16]. This mechanism dominates for the case of Ga, In and possibly Bi in silicon. An example of cell structure is shown by the TEM micrograph of the high dose In implanted crystal of Fig. 3. The interior of each cell (average diameter ~450 Å) is an epitaxial column of silicon extending out to the surface. Trapped substitutionally within the

Fig. 4. Cracks in the near surface region of ^{11}B (35 keV, $6 \times 10^{16}/\text{cm}^2$) implanted Si after laser annealing.

lattice of these columns is the substitutional In in the near surface region. Surrounding each column of silicon is a thin wall ($\sim 50 \text{ \AA}$ thick) containing large concentrations of segregated In. The nonsubstitutional In (see the profiles of Fig. 3) is contained in the cell walls which penetrate to a depth of $\sim 1000 \text{ \AA}$. The instability which leads to lateral segregation and the formation of a cell structure is due to constitutional supercooling at the interface during regrowth. Constitutional supercooling during solidification is well recognized and has long been studied in crystal growth experiments at normal growth velocities [17]. In pulsed laser annealing, effects due to constitutional supercooling are observed on a much finer scale due to the high velocity of the liquid-solid interface. To delay the onset of interfacial instability and to increase C_S^{max} , it is necessary to increase the thermal gradient in the liquid. This implies using higher growth velocities.

In addition to the limitations on substitutional solubility imposed by lattice strain and by interfacial instability during regrowth (constitutional supercooling), there are predicted thermodynamic limits [10] to solute trapping in silicon. Basic ideas underlying these predictions are illustrated schematically in Fig. 5. On a plot of the Gibbs free energy versus composition at fixed temperature, the solidus and liquidus lines intersect at one point, which is the upper limit for the solid composition which can be formed from the liquid at any composition. Plotting the locus of these points at different temperatures on the equilibrium phase diagram defines the T_0 curve, which is the maximum solid composition which can be formed from the liquid at any temperature even at infinite growth velocity. The T_0 curve thus defines the thermodynamic limit to diffusionless solidification. For retrograde systems, thermodynamic arguments given in ref. 10 can be used to obtain a simple estimate for the maximum composition (C_S^{L}) on the T_0 curve. This maximum composition on the T_0 curve is the liquidus composition on the equilibrium phase diagram at the retrograde temperature.

Fig. 5. Schematic representation of the method used to determine the thermodynamic limit to solute trapping (ref. 10).

Predictions [10] of (C_S^L) for five dopants in silicon are listed in Table II and compared with measurements of maximum substitutional solubilities ($C_S^{\max}$) obtained at two different growth velocities. Laser annealing at temperatures of 300 K and 77 K results in regrowth velocities of ~ 4.5 and ~ 6.0 m/sec. At either growth velocity, values for $C_S^{\max}$ are approaching predicted thermodynamic limits for solute trapping. For Ga, In, and Bi, values for $C_S^{\max}$ obtained at a velocity of 6 m/sec are larger by factors of 2-3 than results obtained at a regrowth velocity of 4.5 m/sec. These results are still limited by interfacial instability during regrowth, but they demonstrate that at higher growth velocities the onset of instability can be delayed until higher concentrations accumulate at interface. It is significant to note that at a growth velocity of 6 m/sec the Bi concentration in substitutional lattice sites exceeds the equilibrium solubility limit by more than 3 orders of magnitude.

For the case of As in Si, Table II shows there is no change in the measured maximum substitutional concentration as the regrowth velocity is increased from 4.5 to 6.0 m/sec. This indicates that the thermodynamic limit for As in Si may have been reached. This is reasonable since the determined value for k' is ~ 1.0 (see Table I) which implies that the liquidus and solidus line on the phase diagram are coincident (i.e., the T_0 limit). The fact that the measured value for $C_S^{\max}$ exceeds the predicted thermodynamic limit is probably due to uncertainties on the equilibrium phase diagram from which the predictions were made.

CONCLUSIONS

In pulsed laser annealing of ion implanted silicon, both k' and $C_S^{\max}$ far exceed equilibrium values and both are functions of growth velocity. For B in Si, lattice strain limits the amount of boron that can be incorporated substitutionally to a value of ≤ 4 atomic % without developing cracks in the implanted

region. In the case of Ga, In, and Bi, substitutional solubility is limited by interfacial instability during regrowth caused by constitutional supercooling at the interface. For As in Si, the value for k' is ~ 1.0 and $C_s^{\max}$ is independent of velocity (in the range 4.5 to 6.0 m/sec) indicating that the thermodynamic limit for As in Si may have been reached.

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