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PRECIPITATION IN ION-IMPLANTED AL DURING ELECTRON BEAM PULSED ANNEALING[1]

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We have used TEM and ion channeling to examine the microstructure of Al implanted with Zn or Sb following pulsed electron beam annealing with deposited energies of 0.7-1.6 J/cm^2. The Zn-implanted samples show a high density of dislocations in the near surface region. Zn precipitation is not seen in the electron diffraction patterns. For Sb, randomly oriented AlSb precipitates are observed, and precipitation is inferred to have occurred in molten Al. This is accounted for with the Al-Sb binary phase diagram.

INTRODUCTION

Pulsed annealing of ion-implanted semiconductors has recently received much attention. It is now generally accepted that appropriate pulses can melt the sample surface layer, usually to a depth greater than the implanted ion range, that diffusion of the implanted species then takes place in the liquid phase, and that resolidification occurs by epitaxial regrowth. This can produce an essentially damage-free surface, and in many instances incorporates the implanted species substitutionally in the host lattice(1). Precipitation of second phases after pulsed annealing has been reported only where strong segregation of the implanted species to the surface has occurred(1).

By contrast, few investigations have been made of pulsed annealing of metals. We report here the first study of e-beam pulsed annealing of ion-implanted Al. In the preceeding paper(2), depth profiles of implanted Zn and Sb were examined. The results show that diffusion of both species occurred in molten Al for times up to ∿ 300 nsec. In the present paper,

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we present transmission electron microscopy (TEM) and ion channeling examinations of the near surface microstructure after pulsed annealing. Our choices of implanted species are a very soluble element, Zn and a very insoluble one, Sb.

SAMPLES

High purity Al foils (.005" thick) were degreased and pre-annealed for one hour at 600°C to produce large, damage-free grains (∿ 80 μm). They were then electropolished to a mirror finish and implanted to 1 x 10^{16}at./cm^2 at 150 keV. The implanted surfaces were pulse annealed at SPIRE Corporation with 50 ns (fwhm) electron beam pulses with an average electron energy of 12 keV to produce energy depositions from 0.7 to 1.6 J/cm^2. TEM samples were jet electropolished from the unimplanted side to produce thin sections which included the implanted ions. These were examined in a 100 keV Philips EM201 electron microscope. Ion channeling studies were done on a similarly prepared high purity single crystals by ion backscattering of 1.8 MeV ^{4}He.

Zn-IMPLANTED Al RESULTS

Shown in Fig. 1 are TEM micrographs exhibiting dislocations in the near surface of Zn-implanted Al. The as-implanted sample (1a) showed a dense dislocation array of mixed character (loops and lineal segments).

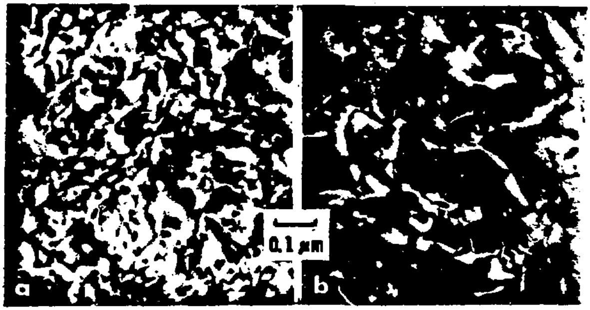

FIGURE 1. (a) TEM micrograph showing dislocations in the near surface of Al after implanting 1 x 10^{16}Zn at 150 keV. (b) Same, but after pulsing with 1.6 J/cm^2.

Pulsed annealing with 1.6 J/cm^2 left the sample grain size essentially unchanged ($\gtrsim$ 80 μm). This and ^{4}He channeling data on a Zn-implanted single crystal annealed with 1.1 J/cm^2 demonstrate that solidification occurs by epitaxial regrowth. After e-beam pulsed annealing with 1.6 J/cm^2 the dislocation density in Fig. 1b is about half of that after implantation. The dislocations seen are predominantly of lineal character. Electron diffraction shows no second phase. ^{4}He channeling experiments on Zn-implanted Al single crystals annealed with 1.1 J/cm^2 exhibit similar amounts of dechanneling in the first 2000 Å below the surface before and after pulsed annealing with 1.1 J/cm^2. ^{4}He channeling results also show that the as-implanted Zn substitutionally of ∿ 90% did not change appreciably.

Thus, both experiments show that the near surface contains a significant dislocation density after pulsed annealing, even though the sample was molten to a much greater depth (∿ 3 μm). The dechanneling depth corresponds reasonably well with that of the Zn; the two are presumably related. The persistance of a significant density of dislocations and the less than 100% substitutionality for the soluble specie Zn differ from results obtained with pulse annealed Si.

Sb-IMPLANTED Al RESULTS

Sb implantation into Al at room temperature produces a dense dislocation network similar to that in Fig. 1a. No AlSb is detected before annealing if the temperature is not allowed to rise during implantation. After pulsed annealing with 1.6 J/cm^2, electron diffraction (Fig. 2a) shows an AlSb ring pattern due to randomly oriented AlSb precipitates within a single grain of Al. A smaller amount of oriented AlSb is also observed. This differs from the predominantly oriented AlSb precipitates observed after conventional thermal annealing of Sb-implanted Al above ∿ 150°C(3). An example from an anneal of 30 minutes at 206°C is shown in Figs. 2C. Fig. 2b and 2d are dark field micrographs with the AlSb precipitates illuminated. The average precipitate diameters are similar, 60 Å and 50 Å, respectively, for pulsed and conventional thermal annealing.

As discussed in the previous paper(2), pulsed annealing results in diffusion of Sb in molten Al. In fact, we also observed such diffusion in a sample in which AlSb precipitates existed prior to pulsed annealing. This requires that Sb be in solution in liquid Al after the pulse. The AlSb ring diffraction pattern contrasts sharply with the oriented AlSb observed when precipitation occurs in the solid phase; we infer from it that substantial precipitation occurred within molten Al.

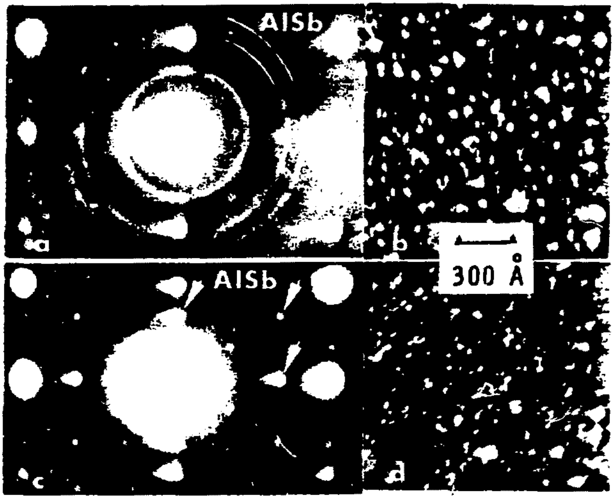

FIGURE 2 TEM diffraction and dark field results for Sb-implanted Al after pulsed e-beam (a and b) and thermal (c and d) annealing. Superimposed white arcs indicate the position of (111), (220), and (311) AlSb diffraction rings in (a) while oriented reflections from the same planes are indicated in (c).

These observations can be understood by considering the equilibrium phase diagram(4) for Al-Sb in Fig. 3. Our peak concentration after pulsed annealing is $C_p \simeq 2.0$ at.%, which exceeds the eutectic concentration $C_{eu} = 0.25$ at.%. During the pulse the implanted region is heated into the single phase liquid part of the diagram, Sb is solutionized, and diffusion occurs. As the implanted region cools, the two phase regime is entered and precipitation of solid AlSb within liquid metal is anticipated for times longer than the nucleation time. For $C_p \approx 2.0$ at.%, the regime occurs between $657°C < T \lesssim 770°C$. Since this temperature range exceeds the melting point of pure Al (660°C), the near surface should enter the two-phase regime before the solid-liquid interface arrives. We estimate that a minimum time in the two-phase regime of ~ 10 ns would be required for Sb diffusion in liquid Al to produce our observed ~ 60 Å precipitate diameter. As the near surface continues to

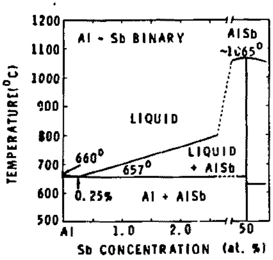

FIGURE 3. A portion of the Al-Sb phase diagram(4).

cool, the liquid-solid interface passes through the implanted layer and the precipitates are frozen in the random orientation that they had while in the liquid.

We have also examined Sb-implanted Al which was pulse annealed with lower deposited electron energies. At 1.1 J/cm^2 precipitates with a random orientation are also observed, thus indicating precipitation within molten Al. At 0.7 J/cm^2, the sample was not uniform; some areas indicated precipitation within the melt, while others did not. From this we infer that 0.7 J/cm^2 is just able to melt the near surface, but inhomogeneities in the electron beam give unmelted areas.

Our observation of precipitates after pulsed annealing differs from most observations on implanted Si, where the impurities remain in supersaturated solid solutions. However, the explantation we have given for precipitation within molten host material is consistent with the observations in Si since those impurity concentrations did not exceed their associated eutectic concentrations. This applies to our Al-Zn observations also because our concentrations(2) (1-2 at.%) do not exceed the liquid eutectic concentration (88.7 at.%)(4). The explantation is also consistent with recent results demonstrating the removal of phosphorous precipitates in Si after laser pulsed annealing(5). In that study the near surface is presumably heated into the single phase liquid region where the P is dissolved from the precipitates and is solutionized. Phosphorous precipitation within molten Si is not expected because the concentration is less than the eutectic concentration. Precipitation after resolidification is probably inhibited for all the impurities studied in Si due to the much lower diffusivities in the solid. In pulsed annealing studies of Cu-implanted Si, precipitates have been observed(1). However, the strong segregation of Cu to the near surface restricts attempts at interpretation with equilibrium phase diagrams. In a recent study Sb-implanted Al was laser annealed, but no AlSb precipitation was detected(6). The failure to observe precipitates could have resulted either from insufficient sensitivity of their x-ray diffraction measurements or a more rapid cooling of the laser pulsed samples through the two phase region such that precipitates did not have sufficient time for nucleation and growth.

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