PRECIPITATION OF COPPER IN SILICON BICRYSTALS

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PRECIPITATION OF COPPER IN SILICON BICRYSTALS

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Résumé : La précipitation du cuivre a été étudiée par microscopie électronique par transmission dans un bicristal Σ25 de silicium. Après un recuit à haute température suivi par un refroidissement rapide, des précipités apparaissent dans le plan du joint. Les réflexions supplémentaires peuvent être indexées dans le réseau de la phase CuSi η'ou dans un sous-réseau de la phase β. Deux relations d'orientation sont observées.

Abstract Investigation of copper precipitates has been carried out in a Σ25 silicon bicrystal by transmission electron microscopy. Orientated precipitation occurs after high temperature annealing and fast cooling. Extra spots can be indexed using the lattice of η'-CuSi phase, lattice related to this of the β phase. Two orientation relationships are found.

1 - INTRODUCTION

Copper is a fast diffusing atom in silicon : near the melting point, diffusion coefficient rises to 10^{-5} cm^{2} sec^{-1} and it is strongly temperature dependent /1/. This causes supersaturation and the formation of precipitates upon cooling. Formation of CuSi particles has been the subject of numerous investigations and growth models have been proposed /2,3,4/. Colonies of precipitates are observed if the cooling rate is greater than 1°C sec^{-1}.

Several crystal structures of copper precipitates have been proposed: Salama /5/ found bcc β Cu-Si, a = 2.85 Å and observed that the presence of dislocations or of SiO_2 particles enhanced the copper precipitate formation. Das /6/ identified a diamond (B_3) Cu-Si phase with a lattice parameter equal to 5.72 Å : the structure can be derived by replacement of closed packed layers by copper atoms.

Solberg/7/ has found the Cu_3Si equilibrium phase in its low temperature polymorph η''. η'' phase has a large orthorhombic unit cell(a = 76.76 Å, b = 7.00 Å, c = 21.94 Å)and originates from periodic displacements of atoms in the intermediate η' phase (trigonal, a = 4.72 Å, γ = 95.72°). The high temperature η phase (trigonal, a = 2.47 Å , γ = 109.74°) is a disordered ,nearly body centered cubic phase.

Like dislocations, grain boundaries (G.B.) can act as nucleation centers for precipitates. It has been shown that, after annealing at high temperature, precipitates appear at G.B. and that they contain copper and nickel /8/. We have studied by T.E.M. precipitates in a Σ25 intentionally doped bicrystal. Electrical properties of this bicrystal are very sensitive to this precipitation /9-11/.

2 - EXPERIMENTAL

The samples used are Czochralski grown Σ25 silicon bicrystals orientated by Aubert and Bacmann at LETI(Grenoble, France)/12/. They are doped with phosphorus ($n = 10^{14}$ at cm^{-3}) and their metallic impurity concentration is lower than 10^{12} $at.cm^{-3}$. Oxygen and carbon concentrations were measured by I.R. spectroscopy :

$$[O] = 0.75\ 10^{17}\ at.cm^{-3}\ ;\ [C] = 5\ 10^{17}\ at.cm^{-3}$$

Disks, 3 mm in diameter, were cut with G.B. going through the center and perpendicular to the plane. Copper was electrochemically deposited on the bicrystal. The heat treatment (900°C, 24 h) was carried out under N_2 atmosphere in a silica tube. Electron transparent foils were obtained by mechanical polishing to a thickness lower than 40 μm followed by ion milling thinning to perforation; electron micrographs were taken at 120 kV in a JEOL 120 CX.

3 - RESULTS

Before annealing or after a slow cooling, G.B. does not contain any defect. After a fast cooling (> $1°C.sec^{-1}$), precipitates appear at G.B. (Fig. 1). We can distinguish two classes: isolated precipitates and colonies. The first appear as black areas, 100 Å wide. Their structure is unknown because they do not give any extra spots by electron diffraction.

Colonies look as nearly circular disks, 1 μm in diameter. All the precipitates are in the G.B.(fig.1). Contrasts show that precipitates generate mechanical strains in the silicon crystals. Extra spots are observed when the selected area encloses one colony. Dark field electron micrographs show that the precipitates are the diffracting objects (Fig. 2) and that they have different orientations in a colony.

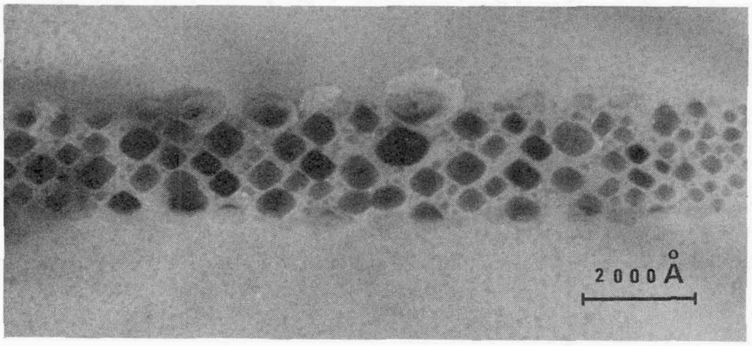

Fig. 1: Colony of precipitates

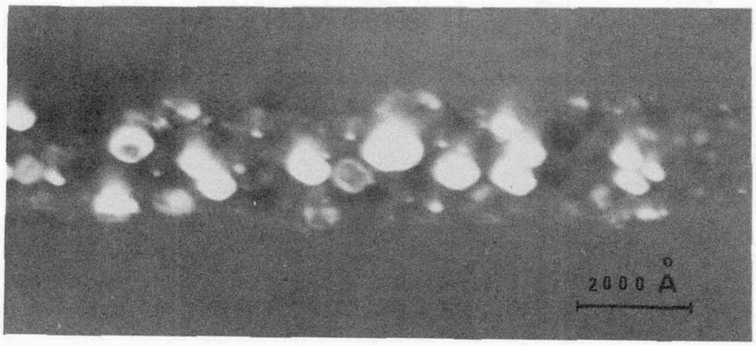

Fig. 2: Dark field micrography of a colony

The number of extra reflexions is low after elimination of multiple scattering. Among them, we observe nearly forbidden silicon reflexions as (200) : in the bulk or in areas free from colonies, they are too weak to be observable. Silicon reflexions were used to measure accurately the reciprocal vector lengthes and angles: all of them can be indexed using the Solberg's $\eta' Cu_3Si$ lattice. However numerous expected reflexions are not observed : they can be either too weak or the precipitates are only partly ordered and some reflexions are missing.

Only two η' reciprocal vectors are nearly parallel to Si reciprocal vectors :

$$(10\bar{1})_{\eta'} \parallel (200)_{Si1} \parallel (200)_{Si2}$$
$$(211)_{\eta'} \text{ or } (2\bar{1}0)_{\eta'} \parallel (111)_{Si}$$

Using diagrams were several extra-spots appear we found two orientation relationships: in the first, we have the two relations:

$$(10\bar{1})_{\eta'} \parallel (100)_{Si1}$$
$$[101]_{\eta'} \parallel [001]_{Si1}$$

In fact, the second relation is not exact: the two directions make an angle equal to 5°. But the relation:

$$(2\bar{1}0)_{\eta'} \parallel (1\bar{1}1)_{Si2}$$

is nearly exact (δ = 4.0°).

The second orientation is deduced from the first by a 90° rotation around $[001]_{Si}$.

4 - DISCUSSION

In a Σ25 bicrystal, the two crystals have a common (071) reticular plane. One crystal transforms into the second by a 16.26° rotation around the common axis $[100]_{Si}$. The two-dimensional lattice cell is large in a $(071)_{Si}$ plane but in each crystal, it exists a $(010)_{Si}$ plane at an angle equal to 8.13°.The Cu_3Si-Si interface is not known; nevertheless, we compared the two-dimensional lattice cells

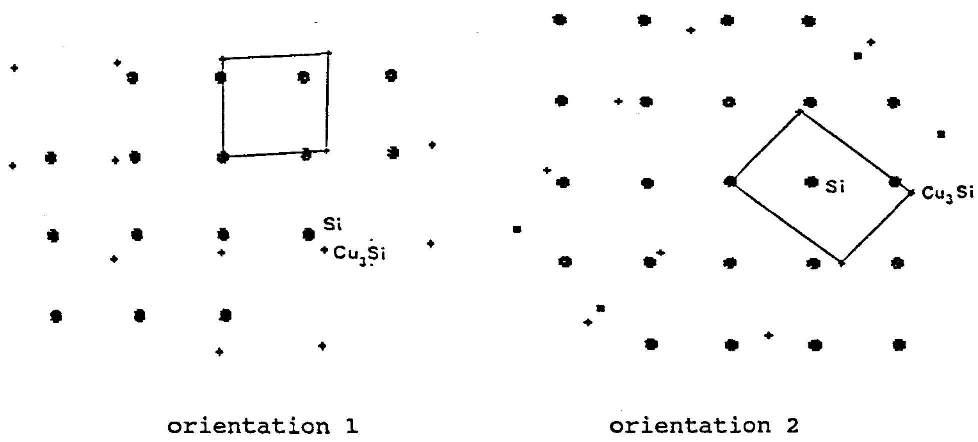

Fig. 3: Drawing of the planar unit cell in the vicinity of the GB plane

of the precipitates in a reticular plane neighbouring the G.B. plane with the square (010)Si cell (figure 3): they are not equal and if the interface plane is the G.B. plane, it must contain many dislocations then epitaxial growth is not likely. For both orientations, the 2 unit cells are similar and this fact could explain the observed orientations.

The 2D-unit cells have the following parameters:

orientation 1:

$a = b = 4.73$ Å $\quad \alpha = 95.7°$

The vectors (11) and ($1\bar{1}$) are perpendicular and nearly parallel to silicon quaternary axis.

orientation 2:

$a = 4.73$ Å $\quad b = 6.35$ Å $\quad \alpha = 98.5°$

$\eta'Cu_3Si$ has a trigonal symmetry, precipitates and Si crystals have no common symmetry axis: in comparison with each Si crystals, precipitates have 24 equivalent orientations. Only two orientations have been observed. More likely, we must refer to the symmetry of the bicrystal: they are only 4 equivalent orientations for each of the 2 cases.

The η'phase is intermediate between the disordered high temperature η phase with a distorted bcc atomic arrangement and the low temperature η'' phase. Solberg /4/ deduced the composition Cu_3 Si from the precipitate growth mechanism ; this result is not surprising : η phase is also on the Si rich side of the Cu-Si phase diagram /13/. Occurrence of the η' phase (instead of the low temperature η'' phase) can be related with the fact that precipitates are observed only after a fast cooling. But the η' lattice is in fact a sublattice of the η phase, bcc with a parameter $a = 2.85$ Å : it is nearly the same lattice as the one of the β phase. We do not know precipitate chemical composition. The observed precipitates could then also be crystallographically related to the β phase, and we would then be able to explain why they appear only after a fast cooling : β Cu-Si exists only if temperature is between 852°C and 754°C. If it is not stable at low temperature, Cu could diffuse in the bulk when T is lower than 754°C, and precipitates disappear when the cooling rate is too low. The few number of observed reflexions indicates a partially ordered structure and the precise determination of atomic arrangement would need an accurate chemical analysis: the method used by Solberg cannot be extended to the case where precipitate takes place at a G.B. Then the Cu-Si precipitates lattice is related to the β-CuSi and to the η'-Cu_3Si lattice.

5 - CONCLUSION

After diffusion of copper and fast cooling, precipitation occurs at $\Sigma 25$ in silicon bicrystals. Electron diffraction extra reflexions can be indexed using the lattice of the η' Cu-Si phase related to the β-CuSi lattice. Several equivalent orientation relationships are found and they correspond to similar, but different two dimensional lattice cells in reticular planes neighbouring the G.B. plane.

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