MICROSTRUCTURES OF Si SURFACE LAYERS IMPLANTED WITH Cu

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ABSTRACT

The microstructures of Si ion-implanted with Cu have been characterized by TEM after annealing. For 1.2 at.%, the Cu is trapped at planar defects, but for 10 at.%, η -Cu₃Si forms and Cu diffuses at its equilibrium solubility. These observations allow proper evaluation of the binding energies of Cu to previously formed internal cavities (2.2 eV) and η -Cu₃Si (1.7 eV). The 10 at.% Cu layer promotes oxidation of Si catalyzed by η -Cu₃Si. The microstructures also indicate that Si implanted with ~2 at.% Cu reforms epitaxially with embedded defects after 8 hr. at 700°C, but for ~10 at.% Cu, epitaxy is not recovered after 6 hours at 600°C.

INTRODUCTION

Advanced Si devices often require high purity to perform properly. The transition metals are an important class of detrimental impurities in Si [1], for which impurity levels $< 1 \times 10^8/\text{cm}^3$ are projected to be required. We have examined Cu as an example, and used ion-implantation to characterize its binding on the walls of cavities in Si formed by prior implantation of He to greater depths [2-4]. Here, microstructures of the implanted layers as determined with transmission electron microscopy (TEM) at 200 keV, and with Rutherford backscattering spectroscopy (RBS) are presented to evaluate the transport of Cu to the cavities properly. At low concentrations (< 1.2 at.%) Cu is bound to defects in the layer that inhibit its transport, but at 10 at.%, η -Cu₃Si forms, allowing Cu diffusion into Si at its equilibrium solid solubility. Knowing the precipitation and solution behavior of the Cu has allowed us to determine that the cavities bind it more strongly (2.2 eV w.r.t. solution) than does Cu silicide (1.7 eV) [3,4]. Moreover, cavity trapping is more effective than silicide precipitation gettering mechanisms currently in use [5] since it is expected to operate at concentrations far below the solid solubility.

Copper is also being evaluated as a possible new metallization for Si microelectronic devices [6]. That application would increase the importance of effective gettering and the need to understand the reactions occurring with Cu on the surface of Si. We find that Cu implantation to 10 at.% promotes rapid oxidation of Si. We identify η -Cu₃Si at the oxide/Si interface, which implies that it catalyzes the oxidation, as discussed by others [7,8]. The microstructures also indicate that the amorphous layer existing after implantation crystallizes and reforms epitaxially with embedded defects at for 1.2 at.% Cu, but epitaxy was not recovered at 600°C for 10 at.%.

LOW Cu CONCENTRATIONS

Specimens of (100) Si were first implanted with 1×10^{17} He/cm² at 100 keV and annealed 1/2 hour at 700°C to form cavities at a depth of 0.3 μm and outgas the He [9]. Specimens were then implanted with 1×10^{16} Cu/cm² at 150 keV, which gave a peak concentration of 2.5 at.% at 74 nm. Annealing for 8 hours at 700°C reduced the peak to 1.2 at.% Cu, which still greatly exceeds the solid solubility of Cu (2×10^{-5} at.%) [10], and trapped 0.5×10^{16} Cu/cm² at the deeper

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Figure 1. a) [100] diffraction pattern from Si implanted with 1×10^{16} Cu/cm² at 150 keV and annealed 1/2 hour at 700°C, showing type a and b reflections. b) Bright-field image of defects; arrows show the two types.

cavity layer. This observation demonstrates Cu binding to the cavities, but transport to them proceeded much more slowly than expected for the rapid interstitial diffusion of Cu in solution at its solid solubility. Similar results with low Cu concentrations were found at other temperatures.

The low transport rate can be understood from the microstructure of the Cu layer determined with plan-view TEM. Electron diffraction patterns exhibit strong reflections from the single-crystal Si matrix, as for the [100] zone in Fig. 1a. Although extra spots are seen, they do not match a copper silicide. The elongated spots (one is labeled "a") near to the {022} matrix spots have an atomic spacing matching {111} Si (3.14 Å). The similar spots closer to the origin were determined by tilting and superposition of patterns to be multiple reflections of the type a and strong matrix reflections, and are not additional reflections. Weak but sharp spots (one is labeled "b") are found at {002} positions (2.72 Å), halfway to the {004} spots; streaks pass through them along the <001> directions. Figure 1b shows two sets of platelet defects corresponding to the two types of extra reflections. Each set has two orientations of linear features at 90° to each other; the two sets are rotated 45° with respect to each other, as are their two types of extra reflections noted in Fig. 1a. With dark-field imaging, each set could be associated with one type of extra spot. The type a features appear to be platelets seen "edge-on" and are 20-130 nm long and 5-13 nm thick. They are apparently misoriented Si platelets resulting from crystallization of the amorphous layer that have not reoriented with the substrate and remain embedded in the single-crystal matrix. The type b features are also platelets, 12-60 nm long and 1-5 nm thick. The streaks through their reflections suggest that they may be twin-related defects.

The RBS spectrum clearly indicates that Cu is in the layer. If Cu silicide were present, we would expect to detect it even at 1.2 at.% since it would align with the matrix and give spot patterns of finite intensity [11,12]. The Cu is apparently trapped as individual atoms at the numerous matrix defect interfaces. Without silicide, Cu may be in solution below its solid solubility; defect trapping would further reduce its transport rate. Finding half of the Cu at the cavities indicates that they bind it more strongly than the defects and can getter Cu from them.

HIGH Cu CONCENTRATIONS

A second type of (100) Si specimen was prepared by increasing the fluence to 1×10^{17} Cu/cm² at 150 keV. In these specimens, Cu diffused to cavity traps at a rate consistent with its diffusivity and solubility in Si until they saturated. After annealing 6 hours at 600°C, the Cu profile peaked at 10 at.% at a depth of 62 nm. Initially, specimens were stored in ambient air and appeared "hazy" to the eye within a day after annealing or ~3 days without annealing. The haze appeared more slowly in similar (111) specimens, e.g. ~20 days. The haze is due to Si-O particles on the surface. The particles are 0.1-0.2 μ m as seen in the secondary electron image in Fig. 2, obtained with the TEM's scanning unit. The microdiffraction pattern in Fig. 2b from a large particle suspended over a hole in the thinned specimen has broad, diffuse rings indicating amorphous material. Other particles have areas that change contrast during tilting and sharp spots superimposed on the ring pattern, indicating that they contain crystallites. Energy dispersive characteristic x-ray spectra from suspended particles showing no crystallites gave spectra with strong Si and O k_{α} peaks and almost no Cu; the C k_{α} peak was detected, apparently due to beam contamination. Thus the particles are amorphous silicon oxides. Such particles are not present on any of our other Si samples, only those implanted with high fluences of Cu.

Electron diffraction analysis identifies the material between particles as polycrystalline Si and η -Cu₃Si. A pattern from a thin area is shown in Fig. 3. Phase analysis is done first by excluding the rings of randomly oriented Si (arrowed); Table I lists the atomic spacings measured for the remaining rings along with those of matching phases in column 1. Identification of the silicide is complicated by two ordering transformations expected as η -Cu₃Si cools from 600°C to room temperature ($\eta \rightarrow \eta' \rightarrow \eta''$) [13]. Solberg [11] examined electron diffraction patterns of room temperature η'' and deduced a large, ordered orthorhombic unit cell (76.76 Å, 7.00 Å, 21.94 Å). His single-crystal patterns imply very many rings but with unknown intensities. A key to the identification is noted by Weber et al. [12]: Solberg's structure has a hexagonal sublattice that accounts for strong reflections. They fit their and Solberg's data to obtain $a = 4.04$ Å, $c = 2.44$ Å.

Figure 2. a) Secondary electron image of oxides on (100) Si implanted with 1×10^{17} Cu/cm² at 150 keV and annealed 6 hours at 600°C. b) Diffraction pattern from an oxide particle (two exposures).

Figure 3. Electron diffraction pattern from thin area of Si implanted with 1×10^{17} Cu/cm² at 150 keV and annealed for 6 hours at 600 °C. Rings due to Si are arrowed; remaining rings are listed in Table I.

Table I. Diffraction Spacings and Intensities. Observed (excluding Si) and Expected [12,14]

d (Å)	Intensity Completeness	Hex. Cu ₃ Si (Å) Ref. [12]	η-Cu ₃ Si (2.23-2.24) [14]
3.50	very weak, partial ring	3.50 (1010)	
3.24	very weak, partial ring		
2.84			2.875 strong
2.45	weak, full ring	2.44 (0001)	
2.31	weak, partial ring		
			2.226 strong
2.12	medium, partial ring		
			2.057 very strong
2.02	strong, full ring	2.02 (1120) 2.03 strong	2.022 strong
		2.00 (1011) 2.01 strong	1.993 strong
	(overlaps Si (1920))		1.893 very strong
1.85	weak, partial ring		
1.79	weak, partial ring	1.78 (2020)	
	(overlaps Si (1860))	1.86 (1121)	1.767 strong
1.48	medium, partial ring	1.42 (2021) 1.43 strong	1.473 weak
			1.318 weak
1.22	weak, partial ring	1.22 (0002)	1.250 strong
1.17	medium, full ring	1.17 (3030) 1.17 strong	1.172, 1.165 weak
			1.158 strong

We used a diffraction simulation program to calculate atomic spacings for this lattice, which are listed in column 2; also given are the four intense reflections of by Weber et al. [12], which

match our most intense rings. The hexagonal lattice accounts for the prominent rings and some less intense ones, as well as others reported earlier [14] (column 4). Atomic ordering apparently produces the additional reflections in column 1. On this basis we conclude that η -Cu₃Si (or related η' or η'') has formed in the implanted layer. Diffraction patterns from thicker areas show the [100] Si zone and the "type a" spots seen with the lower Cu concentration in Fig. 1a.

The nature of the polycrystalline layer and the role of η -Cu₃Si in oxidation are more apparent from cross-section images like Fig. 4a. This specimen was kept under high vacuum ($<5 \times 10^{-7}$ torr) except during thinning for TEM. Nonetheless, amorphous oxide particles protrude above and extend beneath the surface. Between them, the layer has a well-defined depth, 0.25 μm , with lateral crystal sizes 0.1-0.6 μm ; some crystals exhibit twinning. A defected region beneath the layer exhibits strain contrast in other images. The Si grains dominate the images and make identifying specific Cu₃Si grains difficult. Identifying silicide grains within the layer is complicated by the many boundaries and overlapping crystals that give multiple diffraction. However, η -Cu₃Si particles can be identified at the edges of the oxides. Tilting them into contrast and diffracting from a 1/4 μm diameter selected area gave patterns with spots indexing to η -Cu₃Si reflections in Table I but not Si. A row of spots in Fig. 4b matches $(10\bar{1}0)$, $(20\bar{2}0)$ and $(30\bar{3}0)$ in the hexagonal notation. Dark-field imaging with these spots illuminates silicide particles around the edge of the oxide particle, as seen in inset Figs. 4c and 4d. Note that this silicide was carried beyond the original layer depth by the oxide growth. Finding η -Cu₃Si at the oxide/Si interface means that it can promote oxidation as well as furnish Cu into solution in substrate. However, the amount of Cu₃Si at these interfaces is less than expected for 10 at.% Cu. Additional silicide apparently lies within the polycrystalline layer.

Figure 4. a) [011] Bright-field cross-section TEM image of (100) Si implanted with 10 at.% Cu, showing oxide particles growing inward from the surface. b) Electron diffraction pattern from grain in c) identifying it as η -Cu₃Si. c), d) and e) Dark-field images of η -Cu₃Si grains around Si-O particle, in areas indicated correspondingly in a).

SUMMARY AND CONCLUSIONS

Implantation of Cu into Si followed by annealing at 600°C results in η -Cu₃Si formation provided the Cu concentration is high enough (~10 at.%). Its presence is consistent with the transport rates of Cu to internal cavities and allows its binding energy to the silicide phase to be evaluated, 1.7 eV/atom, which is less than the binding energy to cavity walls, 2.2 eV/atom. The silicide was not seen at lower concentration (1.2 at.%), where defect trapping is inferred to have inhibited Cu transport to the cavities. The high concentration blocks epitaxial regrowth, giving a polycrystalline surface layer with twinning. The η -Cu₃Si catalyzes rapid oxidation of Si through the layer and into the substrate during exposure to air at room temperature. The phase is probably initially present at the surface since RBS indicates a surface concentration of 4.3 at.% Cu. We find silicide particles carried into the Si substrate during oxidation, as reported by others [8,15]. Visual examination indicates that (100) surfaces oxidize faster than (111), in agreement with other work [7,8]. If Cu is used as a metallization for Si microcircuits, it needs to have effective barriers that prevent its reacting with the Si.

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