

# Distribution and Chemical State of Cu-rich Clusters in Silicon

## Preprint

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# Distribution and Chemical State of Cu-rich Clusters in Silicon

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Copper is a ubiquitous contaminant in silicon-based device technology that can be easily introduced into the bulk of silicon wafers. According to the existing data on solubility and diffusivity of Cu in Si [1-3], at only 425°C the equilibrium solubility of Cu in Si is as high as  $10^{13} \text{ cm}^{-3}$ , and the diffusivity is such that Cu can traverse 220  $\mu\text{m}$  of single crystalline p-type silicon in under 10 seconds ( $\lambda \cong \sqrt{4Dt}$ ). According to the current understanding of the electrical properties and defect interactions of copper in silicon [4, 5], interstitial copper is a shallow donor with relatively benign electrical activity. On the other hand, copper-rich precipitates are known to severely reduce the minority carrier diffusion length by forming bands of states within the silicon bandgap, thereby providing very effective pathways for recombination [6-8]. It is thus of interest to investigate the distribution and chemical state of copper-rich clusters in a variety of silicon materials, including model defect structures and mc-Si solar cell material. For this purpose, we employed a variety of synchrotron-based analytical techniques: X-ray fluorescence microscopy ( $\mu$ -XRF), X-ray absorption microscopy ( $\mu$ -XAS), and X-ray beam induced current (XBIC).

Four types of materials were utilized in this study: Sample 1: Float zone silicon intentionally contaminated with  $(3-4) \times 10^{16} \text{ Cu/cm}^{-3}$  during crystal growth. Float zone crystals were grown at the National Renewable Energy Laboratory (see Ref. 9 for details). The particular crystal growth conditions lead to a high density of structural defects. With no intentional n- or p-type doping, the actual conductivity of the sample was n-type, as evidenced by the rectifying behavior of a thin Pd diode evaporated on the polished and chemically cleaned surface. In  $\mu$ -XRF mapping, irregularly distributed Cu clusters are observed at structural defects (Fig. 1b). This irregular Cu decoration is expected for slow-cooled samples, wherein supersaturated Cu can diffuse to preferred precipitation sites [10]. The observed Cu-rich clusters are strongly recombination-active, as revealed by XBIC (Fig. 1a). Five Cu-rich clusters in this sample were analyzed by  $\mu$ -XAS.

Sample 2: Misfit dislocation heterostructure, consisting of a 2  $\mu\text{m}$  thick n-type  $\text{Si}_{0.98}\text{Ge}_{0.02}$  middle layer between a 2.5  $\mu\text{m}$  n-type silicon bottom buffer layer on a (001) silicon substrate and a 2.5  $\mu\text{m}$  thick n-type silicon cap layer. At the two interfaces between the SiGe and Si layers, a network of 60° misfit dislocations forms parallel to the surface and propagates in the  $\langle 110 \rangle$  directions, intersecting at 90° angles. Copper was intentionally diffused at 800°C. Samples were fabricated at North Carolina State University (U.S.A.) and copper-contaminated at King's College (U.K.); further details of sample preparation can be found in Ref. 11. In  $\mu$ -XRF mapping, Cu-rich precipitates are observed along the misfit dislocations. From the Cu-K $\alpha$  fluorescence map (Fig. 2), one can clearly see the copper contamination along the network of misfit dislocations parallel to the surface, which intersect at 90° angles in agreement with literature observations [12]. The recombination-activity of these precipitates has been well-established by electron beam induced current (EBIC) and XBIC measurements, and is reported elsewhere [11-13]. Two Cu-rich clusters were analyzed by  $\mu$ -XAS in this sample.

Sample 3: Czochralski silicon containing approximately  $1.8 \times 10^6 \text{ cm}^{-3}$  oxygen precipitates and approximately  $1.5 \times 10^{15} \text{ cm}^{-3}$  boron was chosen because of the high density of precipitation sites for metals and high precipitated oxygen concentration. The sample was intentionally contaminated with Cu and annealed at 1200°C in forming gas ( $\text{N}_2 + 5\% \text{H}_2$ ) ambient for 30 minutes. The anneal was terminated by an air cool. In  $\mu$ -XRF mapping, approximately  $\sim 1.1 \times 10^6 \text{ cm}^{-3}$  copper clusters are observed (assuming a Cu-K $\alpha$  attenuation length of 70  $\mu\text{m}$  and an angle of 45° between the sample surface normal and the detector). Although each Cu-rich cluster covers many pixels in the  $\mu$ -XRF map (each pixel =  $7 \times 7 \mu\text{m}^2$ ) to form a disk- or point-like shape, as evidenced in Fig. 3, the average signal strength within the precipitate is low, evidence for the distribution of Cu in the form of many smaller precipitates. Cu nanoprecipitates have been observed

in infrared transmission microscopy [14], TEM [15], and etching experiments [16] to form elliptical, plate-like, micron-sized colonies of along preferred crystallographic orientations. Interestingly, the elliptical Cu-rich microcolonies observed in  $\mu$ -XRF also appear to be aligned to certain orientations within the crystal, as shown in Fig. 3. Although the spatial density of these colonies ( $\sim 1.1 \times 10^6 \text{ cm}^{-3}$ ) corresponds well to the density of oxygen precipitates ( $1 \times 10^6 \text{ cm}^{-3}$ ), the morphology of these Cu clusters appears not to be spherical, indicating that the Cu atoms in this sample preferred not to homogeneously coat the oxygen precipitates, but either used them or their punched out dislocation loops as nucleation sites for Cu microcolony formation. Three Cu-rich clusters were analyzed by  $\mu$ -XAS in this sample.

Sample 4: As-grown, cast mc-Si wafer extracted from near the bottom of the cast mc-Si ingot, where the interstitial oxygen concentration can be as high as  $10^{18} \text{ cm}^{-3}$ . In  $\mu$ -XRF mapping, Cu-rich clusters were located at a grain boundary in the material, together with similar amounts of Ni and less abundant Fe, although no intentional contamination was performed. The  $\mu$ -XRF map in Fig. 4 shows the Cu distribution along a representative region of the grain boundary. Although the cluster sizes were smaller than the x-ray beam spot size of 200 nm, the number of Cu atoms per cluster was determined to fall within the range of  $(3 \pm 1.5) \times 10^7$  by comparison with standard materials. Were all these Cu atoms contained within one large spherical  $\text{Cu}_3\text{Si}$  particle, the diameters of these particles would be around  $100 \pm 15 \text{ nm}$ . However, it is also possible these  $\text{Cu}_3\text{Si}$  molecules are distributed among a colony of nanoparticles as reported in TEM studies of intentionally-contaminated monocrystalline Si [15]. Seven Cu-rich clusters were analyzed by  $\mu$ -XAS in this sample.

Cu K-edge  $\mu$ -XAS scans of the copper-rich clusters in all four samples yielded strikingly similar spectra to  $\text{Cu}_3\text{Si}$  standard material (Fig. 5b, c). It is interesting to note that Fig. 5a reveals that the Cu K-edge absorption onset energy of  $\text{Cu}_3\text{Si}$  matches that of the  $\text{Cu}_2\text{O}$  standard, and not metallic Cu. The Cu K-edge absorption energy shift of  $\text{Cu}_3\text{Si}$  relative to Cu metal is atypical for metal silicides. Iron metal and silicides, for example, have identical Fe K-edge x-ray absorption onset energies, unlike oxidized iron species that have K-edge onsets shifted to higher energies by amounts proportional to the Fe charge state [17]. For Cu, a quantified absorption edge shift is clearly not sufficient for determining a specific oxidation state; instead, one has to match the whole near-edge absorption spectrum with that of a standard.

The abnormal behavior of Cu stems from the unique electronic properties of Cu in Si. Copper dissolved in p-type silicon is well-known to diffuse predominantly as  $\text{Cu}_i^+$ . Recent *ab initio* Hartree-Fock calculations published by S. K. Estreicher [5] indicate that  $\text{Cu}_i^+$  will not diffuse as a compact  $[\text{Ar}]3d^{10}4s^0$  sphere, but rather, it will promote some its electrons from the 3d to the 4sp orbitals to form weak covalent bonds with nearby silicon atoms. Similarly, copper atoms precipitated at certain internal voids are predicted to promote a small fraction of their electrons to 4sp orbitals for covalent overlap with neighboring silicon atoms [5]. Macroscopic studies on and models of the properties of copper silicides have also indicated a hybridization of the valence Cu and Si orbitals [18-21]. The increased delocalization of Cu valence electrons can qualitatively explain the Cu-K absorption edge shift to higher energies: as they are photo-excited out of the atom, Cu 1s core electrons experience a greater Coulombic attraction with the Cu nucleus due to reduced electron screening, and thus require higher x-ray energies for photoionization. The energy-shifted absorption edge of  $\text{Cu}_3\text{Si}$  is thus concluded not to be indicative of copper oxide or silicate formation.

In fact, it is unlikely that Cu forms an oxidized phase in Si, because of the strong binding energy between oxygen and silicon. In effect, Cu cannot “out-compete” silicon for the oxygen, and thus remains a silicide. This effect is confirmed by computer modeling of West *et al.* [22], wherein the local distortion around an interstitial oxygen atom may be sufficient to attract an interstitial copper ion,  $\text{Cu}_i^+$ , but no significant overlap of electronic orbitals (i.e. electronic binding) occurs between the  $\text{Cu}_i^+$  and the  $\text{O}_i$ .

Because of the relatively low binding energy of Cu to  $\text{Cu}_3\text{Si}$  precipitates, clusters of this phase are easily dissolved during heat treatments. Experiments studying this effect are reported in “Aluminum Gettering and Dissolution of  $\text{Cu}_3\text{Si}$  Precipitates in Silicon” by Buonassisi *et al.* in these proceedings.

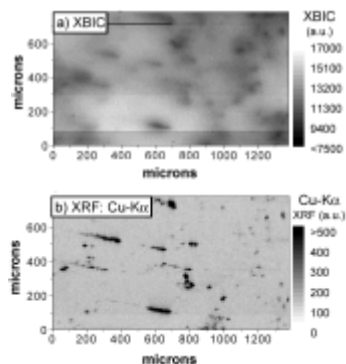
To conclude, the chemical state and distribution of Cu-rich clusters were determined in four different silicon-based materials with varying contamination pathways and degrees of oxygen concentration, including as-grown multicrystalline silicon. In all four samples,  $\text{Cu}_3\text{Si}$  was the only chemical state observed.  $\text{Cu}_3\text{Si}$  clusters were observed at structural defects within all four materials; XBIC measurements revealed that the presence of  $\text{Cu}_3\text{Si}$  corresponds to increased recombination activity. Oxidized Cu compounds are not likely to form in silicon. The +1 eV edge shift in the  $\mu$ -XAS absorption spectrum of  $\text{Cu}_3\text{Si}$  relative to Cu metal is believed to be an indication of a degree of covalent bonding between Cu atoms and their silicon neighbors.

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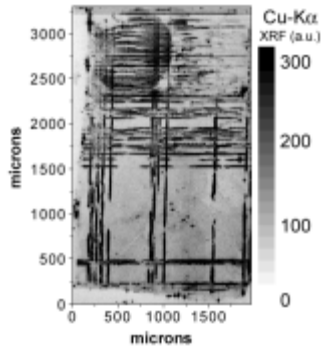
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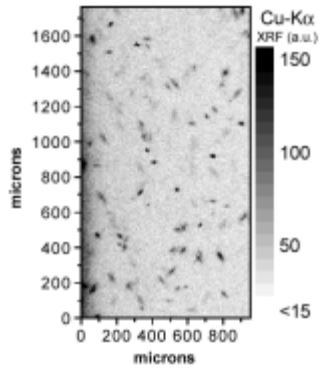
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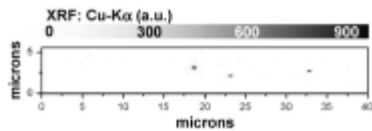
**Fig. 1.** (a) x-ray beam induced current and (b) Cu-K $\alpha$  x-ray fluorescence microscopy maps of float zone silicon contaminated with  $3\text{-}4 \times 10^{16}$  Cu cm $^{-3}$  during crystal growth. Notice the strong correlation between the presence of copper-rich clusters (b) and the decrease of current collection efficiency (a).



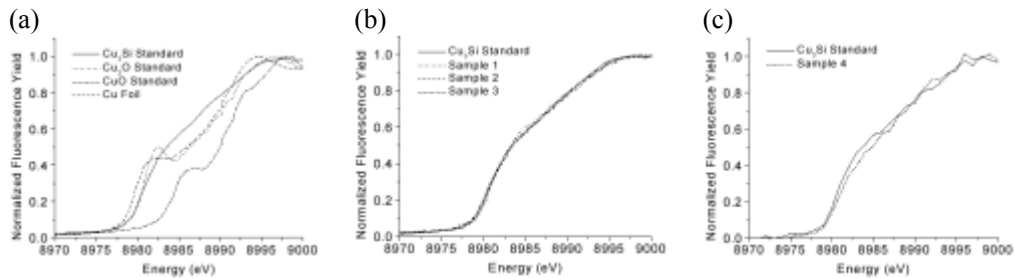
**Fig. 2.** Cu-K $\alpha$  x-ray fluorescence microscopy map of a Cu-contaminated Si<sub>0.98</sub>Ge<sub>0.02</sub>/Si heterostructure. The misfit dislocations parallel to the surface, intersecting at 90°, are heavily decorated with clusters of Cu, confirming the tendency of Cu to precipitate in the vicinity of structural defects.



**Fig. 3.** Cu-K $\alpha$  x-ray fluorescence microscopy map of Cu-contaminated Czochralski silicon with  $\sim 10^6$  oxygen precipitates per cm<sup>3</sup>. Elliptical Cu-rich clusters can be observed, oriented along preferred crystallographic orientations.



**Fig. 4.** Cu-K $\alpha$  x-ray fluorescence microscopy map along a grain boundary of as-grown cast multicrystalline silicon. Despite no intentional contamination, Cu-rich clusters are present.



**Fig 5.**  $\mu$ -XAS showing the spectra of standard materials (a), and then the excellent match of Cu-rich clusters in a variety of silicon materials with the Cu<sub>3</sub>Si standard (b,c, taken at different beamlines). Sample descriptions are provided in Sections II and III. Notice in (a) that the edge onset energy of Cu<sub>3</sub>Si is not coincident with metallic Cu as would be expected from a metal-silicide, but is shifted by +1 eV. This can be understood as an effect of the delocalization of Cu-3d electrons in the presence of Si.

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