Accurate Modeling of Copper Precipitation Kinetics including Fermi Level Dependence

Hsiu-Wu Guo and Scott T. Dunham
Department of Electrical Engineering,
University of Washington Seattle, WA 98195

Copper is one of the most important contaminants in Si technology and it has detrimental effects on device performance and reliability if present in active regions. In this work, we investigate Cu precipitation models that provide the foundation for simulating Cu activation, diffusion, and precipitation processes in silicon. These models are evaluated in terms of their accuracy and computational efficiency. Simulation results are verified by comparison to experimental measurements. Unusual behavior after rapid quenching is reported by Flink *et al.* [1] as shown in Fig. 1, where the remain interstitial Cu concentration equals the initial concentration at relatively low Cu concentration, reaches a maximum, and then starts to drop beyond a critical level which depends on the dopant concentration.

A huge volume change is involved in Cu precipitation process ($V_{Cu_3Si} \approx 2.3 V_{Si}$). Thus for 3D precipitates (e.g., spherical), precipitation must either incorporate vacancies (V) and/or eject interstitials (I). However, self diffusion via point defects is very slow ($E_A \approx$ 4-5 eV) at low temperatures. Thus, stress is minimized via formation of 2-D precipitates (flat disc-shape) [2]. Weber *et al.* [3] reported that positive-charged copper is dominant in silicon, while Cu precipitates must be nearly neutral, due to the Coulombic repulsion.

The nucleation barrier for disc-shaped precipitate can written as:

$$\Delta G_{n_c} = \frac{\gamma^2 \pi \Omega}{dkT[\ln(C_{Cu}/C_{ss}^{i,disc}) - \ln(p/n_i)]} \quad (1)$$

where γ (eV/cm) is the surface/strain energy per unit perimeter, $C_{ss}^{i,disc}$ is the intrinsic solubility associated with planar defects, Ω and d are the volume density and thickness of precipitate. Since the rate of nucleation depends on the exponential of the nucleation barrier, as the material changes from n-type to p-type, nucleation shuts off abruptly. Note that p/n_i and this barrier drop abruptly when C_{Cu^+} exceeds C_{B^-}.

Cu precipitates introduce deep levels, so we assume that Fermi level is pinned at the interface, causing a built-in electric field, repelling Cu^+ near the periphery of the precipitate more significantly in p-type material. Pairing reaction between Cu^+ and B^- is also included.

We model precipitation kinetics via discrete rate equations for evolution of size distribution based on adding a single free atom to an existing precipitate [4]. The driving force for Cu precipitation is due to the difference of free energy, which depends on Fermi level, size of precipitate [5], and concentration of free copper. To increase computational efficiency, Fokker Planck equation [6] is used to describe the discrete system as continuous equation, and then rediscretized more coarsely.

Simulation results are compared to data from Flink *et al* and shown in Fig. 1. Cu precipitates only when C_{Cu} exceeds C_B (e.g., material is n-type). The main reason for this phenomenon is the dependence of solubility, and thus nucleation barrier, on Fermi level (Eq. 1). The remaining copper drops further with increasing initial Cu concentration even though material becomes p-type. This is because precipitate can grow once critical nuclei form. Fig. 1(b) shows the bulk concentration of precipitated copper after sufficient storage time at room temperature to let interstitial copper complete its preferred reaction path: either to diffuse out to the surface or to precipitate in the bulk [1]. Agreement of simulation results and experimental data is excellent.
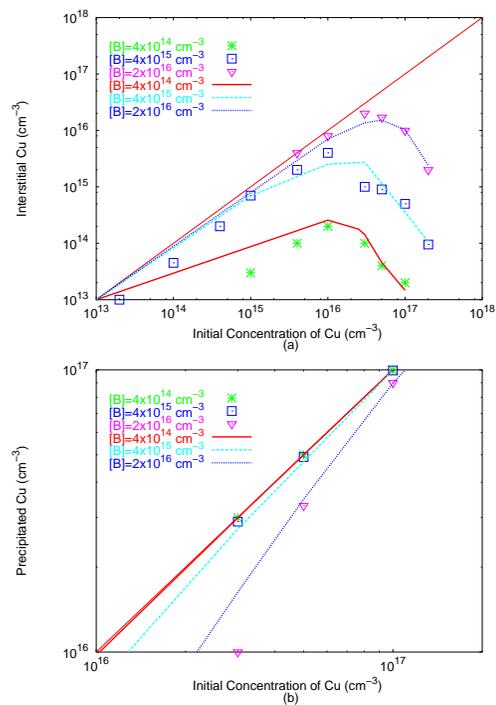

Figure 1: (a): Interstitial copper concentration as measured with TID 30 minutes after quench at room temperature vs. initial concentration of copper at in-diffusion temperature in samples with 3 different B concentrations. (b): Precipitated copper concentration measured with XRF after long hold time [1].

References

[1] C. Flink, H. Feick, S.A. McHugo, W. Seifert, H. Hieslmair, T. Heiser, A.A. Istratov, and E.R. Weber, *Physical Review Lett.* **85**, 4900 (2000).

[2] M. Seibt, H. Hedemann, A.A. Istratov, A. Sattler, and W. Schróter, *Phys. Stat. Sol.(a)* **171**, 301 (1999).

[3] E.R. Weber, *Appl. Phys. Lett.* **A30**, 1 (1983).

[4] S.T. Dunham, *J. Electrochem. Soc.* **142**, 2823 (1995).

[5] S.T. Dunham, *Appl. Phys. Lett.* **63**(4), 464 (1993).

[6] L. Demeio and B. Shizgal, *J. Chem. Phys.* **98**(7), 5713 (1993).