Copper behavior in bulk silicon and associated characterization techniques

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Since the introduction of copper in the semiconductor industry environment, a lot of efforts have been made to efficiently monitor the metal contamination during device processing steps. Standard analytical techniques have been improved and other new methodologies have been introduced to allow copper trace detection with a detection limit in the 10^{10} cm⁻² range. Contamination experiments, which were used to test the feasibility of these methods, have simultaneously yielded new, sometimes unexpected, results on the physical properties of copper impurities in silicon. The electrical methods constitute a particularly important class of trace detection tools since their sensitivity is among the highest and their implementation is relatively easy. Their reliability however strongly depends on an accurate modeling of the copper behavior in silicon. The purpose of the present work is to review recent experimental data on copper in bulk silicon and to discuss their consequences into the field of copper trace detection methods.

First, the physical properties of copper impurities in bulk silicon, upon which the electrical methods rely, are addressed. Well established and up-to-date results on diffusion, solubility, precipitation, electrical activity and defect reactions involving copper impurities are briefly summarized. Unsettled issues which are of importance in the framework of electrical detection, are emphasized. Then, the physical principles, assumptions and recent developments of the electrical methods based either on diffusion minority carrier length and lifetime measurements (1), or transient ion drift (TID) measurements (2) are outlined. Expected performances and limitations of both methods are discussed.

In the second part, recent experimental data obtained by TID on quantitatively contaminated silicon samples are discussed. It is shown in particular that in high quality Czochralski grown silicon crystals, with a low copper contamination level, bulk precipitation or trapping of supersaturated interstitial copper impurities during cooling from high temperatures is almost suppressed. Near surface precipitation and out-diffusion of copper occurs at a sufficiently low rate to leave a significant amount of copper impurities interstitially dissolved even after a standard rapid thermal process (RTP). Also, room temperature stability of supersaturated interstitial copper is found to be considerably higher then expected from previously published data (3), (Fig.1). In float-zone grown silicon wafers however, the residual amount of interstitial copper (Cu_i) after RTP follows a radial distribution (Fig. 2), increasing over one order of magnitude from the center to the edge of the wafer. This behavior is tentatively attributed to trapping of copper impurities by crystal growth defects, such as vacancy clusters. Exposure to visible light of copper contaminated samples is found to reduce temporarily the near surface interstitial copper concentration (Fig.3). This transient effect is tentatively attributed to a photo-induced reduction of the near surface electric field which could enhance the room temperature out-diffusion of interstitial copper. Possible consequences of these results for the copper trace detection methods will be discussed.

REFERENCES

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Fig. 1 : Normalized interstitial copper concentration versus storage time at room temperature. (\blacktriangle) are from Ref. 3.



Fig.2 : Lateral distribution of Cu_i in FZ and CZ after 1 min at 900°C and quench.



Fig.3 : Evolution of the Cu_i concentration during 10 minutes of illumination and subsequent storage in the darkness.