Surface Contamination Removal From Si PV Substrates Using A Biodegradable Chelating Agent and Detection of Cleaning Endpoints Using UV/VIS Fluorescence Spectroscopy.

Mark George[1], David Bohling[1], Helmuth Treichel[1], Avery Goldstein[1], Herbert Litvak[2], Sara Ostrowski[3], Ian Mowat[3], and Werner Kern[4]
[1]Sunsonix Ltd, Milpitas, CA 95035, USA
[2]Lightwind Corporation, Petaluma CA, 94952, USA
[3]Evans Analytical Lab., Sunnyvale, CA 94086, USA
[4]Werner Kern Associates, Lakewood, NJ 08701, USA

Considerable effort has been expended to eliminate contaminants that degrade semiconductor IC performance. These same contaminants have not been adequately addressed in Silicon PV manufacturing processes. More often than not, PV wafers only receive a quick deionized water (DIW) rinse, HF dip to remove native oxide and a final DIW rinse or partial SC1/SC2 cleans. Due to cost pressures, cleaning baths are often used far longer than IC manufacturers would ever consider feasible.

Compounding this issue, neither the DIW rinse nor acid (e.g., HF or HCl) dip are effective at removing transition metal contaminants such as Fe, Ni, Cr, Cu, Zn and others that are responsible for severe degradation of minority carrier lifetime. Photovoltaic efficiency is directly correlated to minority carrier lifetime through increased open circuit Voltage. This is particularly critical within the perspective of the research presented here showing very high surface transition metal contamination on first quality c-Si and mc-Si substrates.

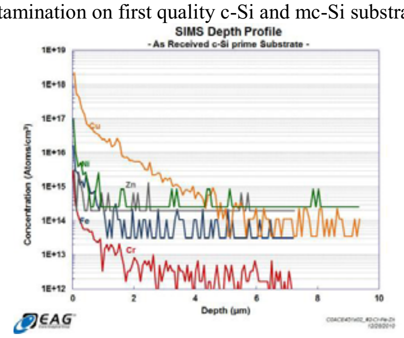

Fig. 1: SIMS depth profile of as-received c-Si prime substrate.

In particular, we have found that very high concentrations of copper (Cu) are present on these substrates in addition to significant levels of the other metals described. The SIMS depth profile shown in Figure 1 is completely corroborated using Surface TOF-SIMS, a highly sensitive and preferred methodology for detection of metal surface contaminants. Although identification of the source(s) is beyond the scope of this paper, this contamination must be removed to ensure maximum solar yield of subsequent devices.

Sunsonix has developed a biodegradable and biocompatible cleaning chemistry (SX-E™) that efficiently removes interfacial transition metals and most metal cations in both HF based surface cleans and SC2 HCl based cleans. The chemistry can also be applied directly in a DIW bath, added directly to a KOH texturing bath, or basically to any rinse step in the complete front end process. This versatility of the chemistry makes the SX-E clean a "drop-in" replacement for existing silicon based photovoltaic manufacturing lines [1, 2, 3].

A striking example of this cleaning is by evaluating surface Cu removal by only 300ppm SX-E addition to a standard DIW rinse and comparing that to the standard without SX-E (Fig. 2). More dramatic results are seen when SX-E is combined with truly engineered cleans designed to maximize surface metal removal, and these will be described in the full paper.

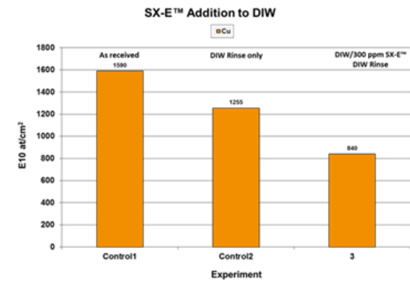

Fig. 2: 300ppm addition of SX-E to DIW rinse reduces surface Cu by 50% versus as-received wafers.

Currently, cleaning bath chemistry becomes depleted over time and number of substrates with little attention paid to differential contamination between subsequent wafer cleaning operations. The authors have collaborated to develop an experimental apparatus used in UV/VIS and fluorescence spectroscopy [4] to determine cleaning bath endpoints (Figure 3). It consists of a hybrid optical absorbance/fluorescence system. The system is capable of measuring optical signals from ~200-900nm, with a spectral resolution of ~2nm.

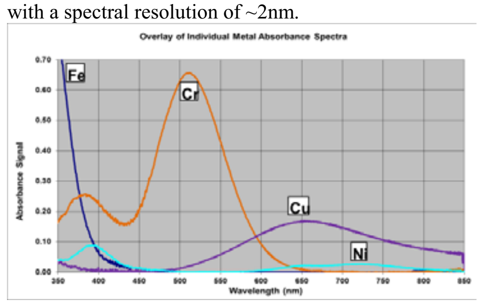

Fig. 3: Optical absorbance signals; Fe has a unique signal <~375nm. Cr has a unique signal at ~ 511nm. Cu has a fairly unique signal at ~ 850nm.

This comprehensive approach to contamination detection, cleaning, and endpoint determination should have a dramatic impact on overall PV manufacturing and has been shown to dramatically improve PV efficiency.

References:

[1] Crystalline Silicon Solar cell Efficiency Improvement by Advanced Cleaning Technology, D. Bohling, H. Treichel, T. Lazerand, A. Goldstein, and M. George, Tech NSTI-Nanotech 2010, Vol. 3, 2010, pp. 704-707

[2] Radiochemical Study of Semiconductor Surface Contamination, Werner Kern, RCA Review 31, pp. 207-264, 1970

[3] T.M. Pan, T.F. Lei, T.S. Chao, M.C. Liaw, F.H. Ko, and C.P. Lu, Journal of the Electrochemical Society, Vol. 148, no6, pp. G315-G320, 2001

[4] D.A. Skoog, F.J. Holler, and T.A. Nieman, Principles of Instrumental Analysis 5th Ed., 1997