

2CO.16.5: OPTICAL SPECTROSCOPY OF CHELATED TRACE METALS FOR WET CLEANING PROCESS CONTROL AND OPTIMIZATION

Herbert Litvak¹, Helmuth Treichel², Avery Goldstein², Mark George², David Bohling²

¹Lightwind Corporation, 621 Second Street, Suite B, Petaluma CA, 94952, USA

²Sunsonix™, 859 Pheland Ct, Milpitas, CA 95035, USA

Corresponding Author: Herbert Litvak, phone: +408-568-033, e-mail: herbert_litvak@sbcglobal.net

ABSTRACT: UV-visible spectroscopy is a technique that readily allows one to determine chemical concentrations of a wide variety of substances over a wide range of conditions. Iron, cobalt, nickel, titanium and copper are important metals that when present on a silicon wafer surface adversely influence the efficiency of resulting PV devices. However, many of these surface ions can be effectively removed during wafer cleaning by the addition of a complexing or chelating agent (such as SX-E™). Since many of the ion-chelate molecular complexes exhibit optical absorption and/or fluorescence in the easily-accessible UV-visible spectroscopy range, they are suitable for chemical analysis by spectroscopic techniques. In this paper, we explore the spectroscopy of several of these metal ion complexes, as well as their potential for chemical analysis and process control, e.g. for endpoint detection, measurement of cleaning bath lifetimes, and as a tool to optimize cleaning sequences.

Keywords: c-Si, Characterization, Experimental Methods, Fundamentals, Photovoltaic, Wet Cleaning, UV/VIS, Fluorescence, Process Control

1 INTRODUCTION

The contamination of the substrate surfaces usually occurs as a result of physical or chemical adsorption by electrolytic action or by exchange of surface atoms with impurity ions in solution [1, 2]. The questions concerning the required bath purity, bath lifetime and subsequent silicon surface contamination can only be answered empirically and or off-line. The need for real-time, on-line chemical measurements is becoming apparent. The addition of a complexing agent to enhance the removal of metallic ions has been used to reduce surface contamination of RCA-derived cleaning chemistries [3, 4]. Historically, these molecules typically feature conjugated double bonds which will generally fluoresce due to delocalized π -electrons. Electron donating groups such as NH_2^- or OH^- enhance fluorescence while electron withdrawing groups such as Cl^- , COOH^- or NO_2^- inhibit fluorescence. This feature of metal complexes to fluoresce is explored as a potential metrology method for direct measurement of metallic ion concentration in cleaning baths.

2 EXPERIMENTAL

UV/VIS Fluorescence/Absorbance analysis is one of the major techniques of modern analytical chemistry. None rival UV-Visible spectrometry for its simplicity, versatility, speed, accuracy and cost-effectiveness, a major plus for photovoltaic cell manufacturing. The experimental apparatus used in this study consists of a hybrid optical absorbance / fluorescence system created by Lightwind Corp. (Petaluma, California USA, distributor of Ocean Optics). A schematic of the apparatus is shown in Figure 1. The system consists of a compact multi-channel optical spectrometer with a sensitized Si CCD detector array, capable of measuring optical signals from ~200-900nm, with a spectral resolution of ~2nm. The spectrometer is coupled to a cuvette sample holder via a silica optical fiber and collimating lens. For optical absorbance measurements, a tungsten-halogen light source was coupled to the sample holder by a second optical fiber and collimating lens. For fluorescence measurements, an additional optical fiber and lens directed fluorescence excitation light from a light-emitting diode (LED) or compact laser to the sample compartment. For some measurements, the optical

fiber and lens were dispensed with, and the LED or laser illuminated the sample directly. All measurements were made with the sample contained in a standard 1cm square cuvette, with appropriate instrument background corrections applied to the data. A flow system for direct sampling of a bath is currently under development.

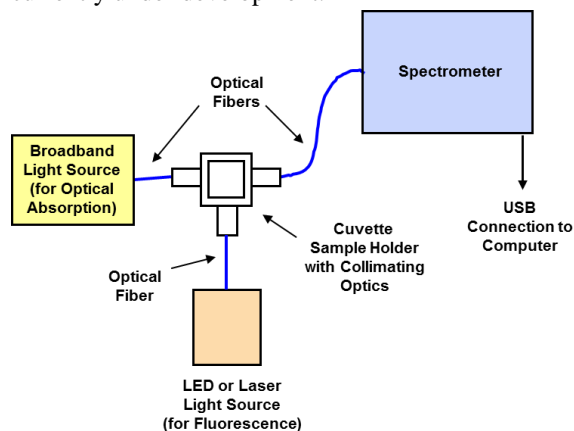


Figure 1: Experimental Setup

Samples consisted of a control and test series using various concentration of the biodegradable chelating agent SX-E™ and various metal standards for Cu, Ni, Cr, and Fe and mixtures thereof. These were prepared in aqueous solutions in ranges from zero to 250:1 chelator to metal ratio. All experiments were carried out at room temperature (~22 °C).

3 RESULTS AND DISCUSSION

Absorbance measurements were made in the ~350-850nm wavelength range on samples of Fe, Cu, Ni, and Cr in buffer solutions containing various amounts of SX-E™. In this study, SX-E behaves both as a complexing agent and as a spectroscopic taggant. Figure 2 is an overlay summarizing the salient features of the absorption spectra of the metal with the SX-E taggant. Fe, Cr, and Cu have strong and distinctive absorption signatures, which allow clear differentiation of the various metals. Ni however is a weak absorber, with an absorption spectrum similar to that of Cu, which could present a challenge in quantitation of Ni in the presence of Cu. However, sophisticated spectral analysis schemes are available, which are expected to reduce this difficulty (see, e.g. Reference 5).

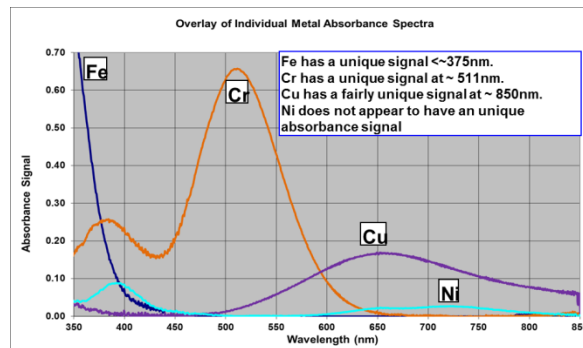


Figure 2: Optical absorbance signals

An interesting feature of this work is the shift in absorbance spectra as the ligand-to-metal ratio changes (see Figures 3a and 3b). This phenomenon may occur as the molecular complex incorporates more SX-E™ molecules for each metal ion, and may involve interesting solvent cage effects, as well.

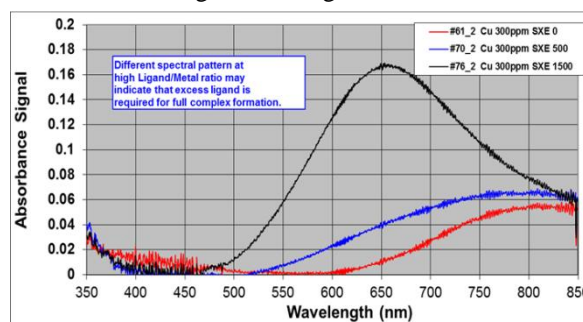


Figure 3a: Shift in optical absorbance spectrum as a function of ligand / metal ratio: Cu.

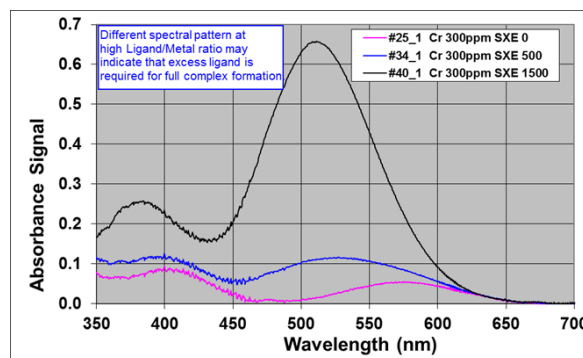


Figure 3b: Shift in optical absorbance spectrum as a function of ligand / metal ratio: Cr.

An important characteristic of any analytical technique is quantitative detection. Figure 4a shows a graph of 380nm absorbance signal for Fe samples at various concentrations in 1000-1500ppm of SX-E™.

The graph shows good linearity from a few ppm to a few 100ppm, suggesting the possibility of sensitive quantitative analysis via absorption spectroscopy into the low ppm region for Fe. Good linear results were also obtained for Ni (Figure 4b), but because of it is a much weaker absorber than Fe, detection limits are not likely to go below ~ 100 ppm with the current instrumentation. Plots of absorbance vs. concentration for Cr and Cu showed non-linear results, perhaps in part caused by the spectral shifts at high SX-E™/metal ratio discussed above.

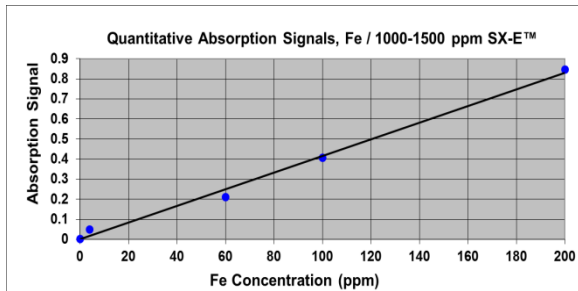


Figure 4a: Quantitative Fe-Determination

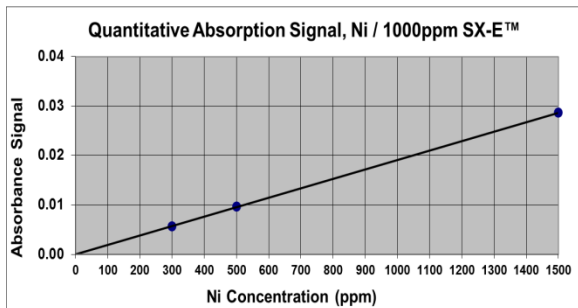


Figure 4b: Quantitative Ni-Determination

Fluorescence spectroscopy is a complementary technique to optical absorbance, and can in principle offer much lower detection limits, because of decreased optical background and interference and far less sensitivity to small variations in the intensity of probing light. Of the metals tested in this study, only Fe exhibited noticeable fluorescence. Figures 5 and figure 6 show normalized fluorescence spectra of Fe samples at various Fe and SX-E™ concentrations (excited by a 385 nm LED). Interestingly, there is a marked shift in spectral shape for samples having SX-E™ / Fe ratios above and below ~ 8.0. This appears to be additional spectroscopic evidence for changing configuration of the Fe / SX-E™ complex as the metal / ligand ratio changes.

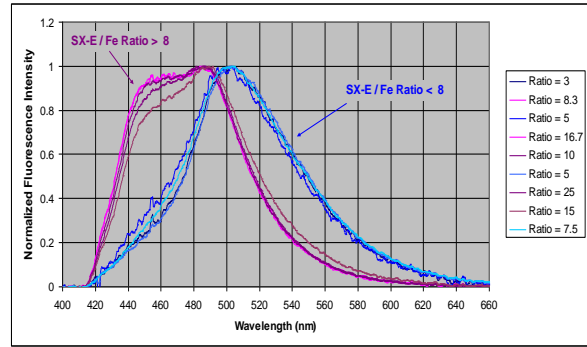


Figure 5: Normalized Fe fluorescence spectra, showing spectral shift at ligand / metal ratio >~8.

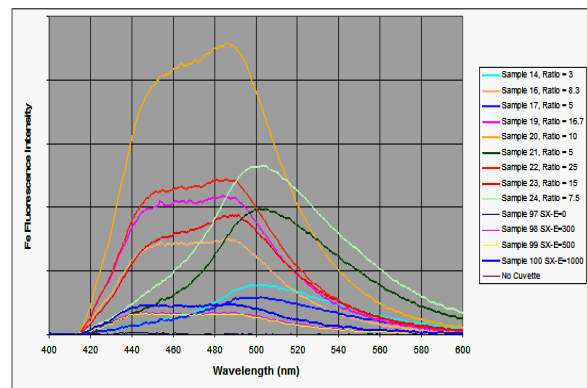


Figure 6: Fe fluorescence emission spectra at various metal and ligand concentrations

A practical example of Fe detection via the fluorescence method is shown in Figure 7, which shows traces of iron from cleaning baths at two different SX-E™ concentrations. The fluorescence spectra are easily detected, even though detection by the optical absorbance method was very difficult, because of the low concentrations. The cleaning experiments were performed on crystalline silicon substrates under identical conditions except changing the taggant concentration. TOF-SIMS data showed Fe surface concentrations of 1-4 E10 at./cm² and Ni surface concentrations of 7-12 E10 at./cm² respectively.

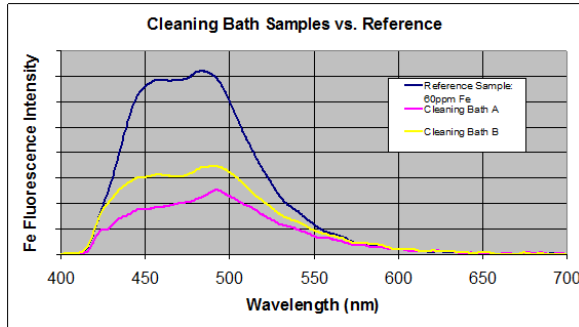


Figure 7: Fluorescence spectrum from wafer cleaning baths at two different SX-E™ concentrations.

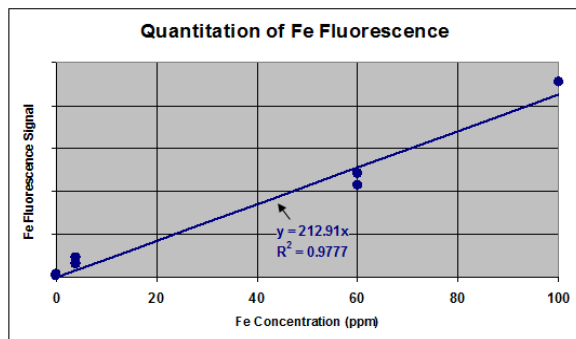


Figure 8: Quantitative Fe detection via fluorescence spectroscopy

Figure 8 shows linear behavior of fluorescence emission signal vs. Fe concentration (Data are for SX-E / Fe ratios $\geq 10/1$). Detection limits are estimated well into the ppb regime; even lower with system optimization.

4 SUMMARY AND CONCLUSIONS

Our studies have shown that UV-Vis optical spectroscopy (both absorbance and fluorescence) has the capability for both qualitative and quantitative analysis of metal ion complexes. The spectroscopic instrumentation lends itself easily to real-time, in situ measurements of cleaning chemistry with regards to its status and efficacy. This in turn allows for a high degree of control of the cleaning process, enabling benefits such as end point (end of process) detection, process fault detection, and timely bath renewal, among others, and will speed the development of new processes, as well as process ramp from lab to pilot line to volume production.

Future work will focus on real-time measurement of bath lifetime (time-to-refresh), and correlation of spectroscopic signals with cleaning efficiency. With the exception of Nickel, the metals which have the most impact on minority carrier lifetime and cell efficiency (Cu, Fe, Cr) all have unique fluorescence and absorption spectra; the SX-E is transparent in this region and does not fluoresce. Although our results are preliminary, we strongly believe that this could readily be developed into a viable end-point/breakthrough analytical tool.

5 ACKNOWLEDGEMENTS

The authors thank Sharyl Maroviov and Henry Miranda for providing access to their wet lab for performing our in-house testing. This project was supported by the US Department of Education and the Arizona Governor's Office of Economic Recovery.

6 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] Removal of trace metals using a biodegradable complexing agent, H. Treichel, A. Goldstein, M. George, D. Bohling, J. Rentsch, A. Oltersdorf, M. Zimmer, S. Ostrowski, I. Mowat, L. Wang & W. Kern, Photovoltaics International, Q2, Ed. 12, pp. 81-93, 2011
- [4] 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
- [5] D.A. Skoog, F.J. Holler, and T.A. Nieman, Principles of Instrumental Analysis 5th Ed., 1997
- [6] P. Pelikan, M. Ceppan, and M. Liska, Applications of Numerical Methods in Molecular Spectroscopy, CRC Press, 1994