August 23, 2004

Ken Zweibel
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401

RE: NREL Subcontract # ADJ-1-30630-12

Dear Ken:

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period
July 03, 2004 to August 03, 2004, under the subject subcontract. The report highlights progress
and results obtained under Task 3 (Si-based Solar Cells) and Task 4 (Diagnostics).

Task 3: Si Based Solar Cells

As discussed in the previous report, the average grain size of in-situ aluminum-induced
crystallized (AIC) Si films correlates well with the time the Al layers remained exposed to air
prior to Si film deposition. Figure 1 shows optical microscopy images of in-situ aluminum-
induced crystallized samples taken through the glass substrates. It has been reported that the
aluminum oxide layer is required for layer exchange process although it is not required for
crystallization process itself. It is reasonable to claim that the oxide layer acts as a physical
barrier forcing the growth of Si grains laterally when they reach the thickness of the initial

aluminum layer. It also acts as diffusion barrier for Si and Al atoms leading to a lower nucleation and thus large Si grains. There has been little attention paid to the characterization of the oxide layer, other than some work from Nast at UNSW [1]. Since the growth of the oxide depends on time between Al and Si depositions. Al surface treatments and Al sample storage, it represents a potentially uncontrolled variable in much of the AIC work.
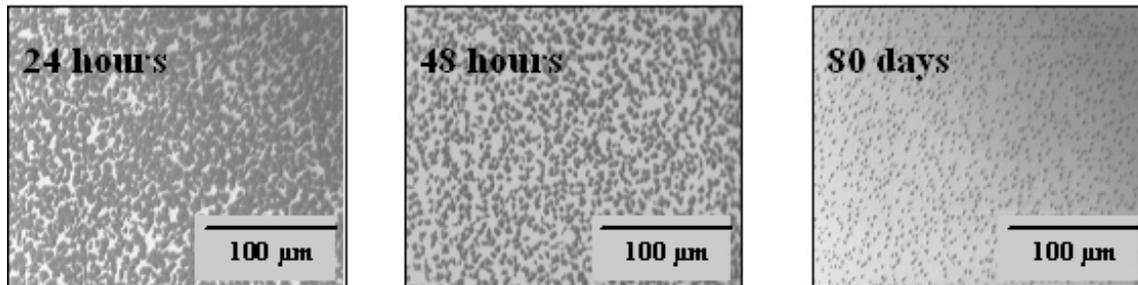
Figure 1 Optical microscopy pictures of partially crystallized Si samples taken through the glass substrate: (a) with Al layer exposed to air for 24 hr before Si deposition, (b) with 48 hrs, and (c) with 80 days.

The oxide surface was monitored over a period of 12 days using spectroscopic ellipsometry measurements. Samples of e-beam deposited Al on glass were stored in air. Although formation of the native oxide layer is thought to be a self-limiting process, ellipsometry results in Figure 2 reveal changes in the optical properties of the oxide layer indicating that its structure may be changing long after the Al film deposition.
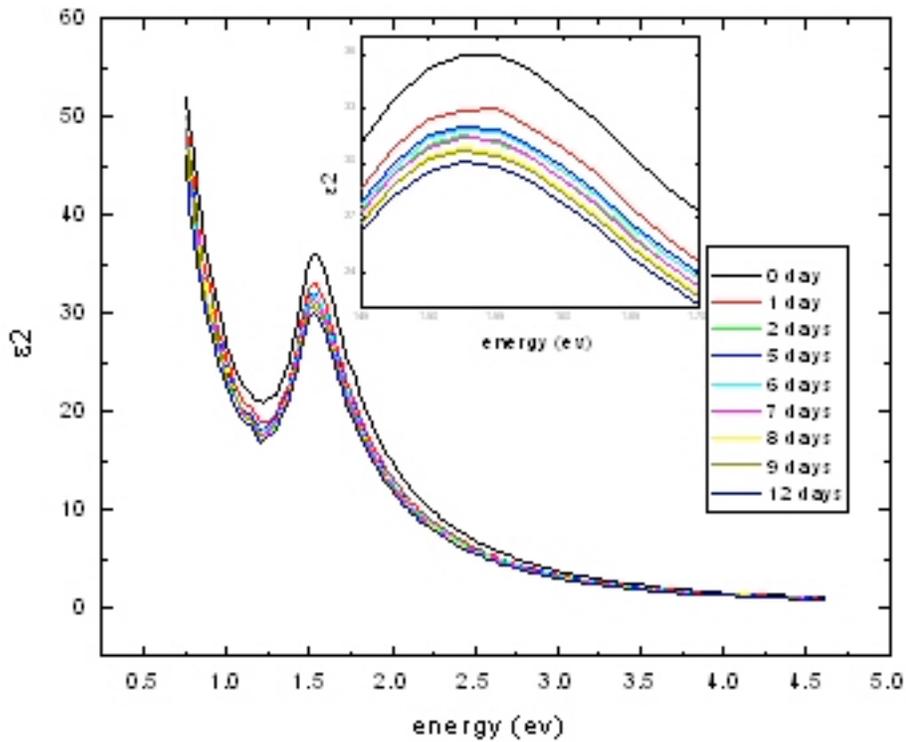
Figure 2 Ellipsometry measurements showing a progressive change in the optical parameter ε_2 of 100 nm thick aluminum layers even after 12 days. Inset shows the decrease in the peak over the range 1.45 to 1.7 eV.

In order to understand the effect of initial aluminum layer on the crystallization and layer exchange process, aluminum layers with different thicknesses were deposited by electron-beam deposition on 7059 glass substrates. XPS and Auger analysis were then performed on aluminum films. As expected, XPS depth profiles showed an oxygen rich surface on the aluminum layers as shown in Figure 3. The plot is normalized with respect to the Al-O peak, which is located at 75.6 eV. As the sputtering depth increases the intensity of the bulk aluminum peak, which is located at 73.0 eV also increases. However, a detailed analysis of the spectra shows a shift for Al-O peak to a lower binding energy as the sputtering depth increases indicating the presence of more than one oxidation state.
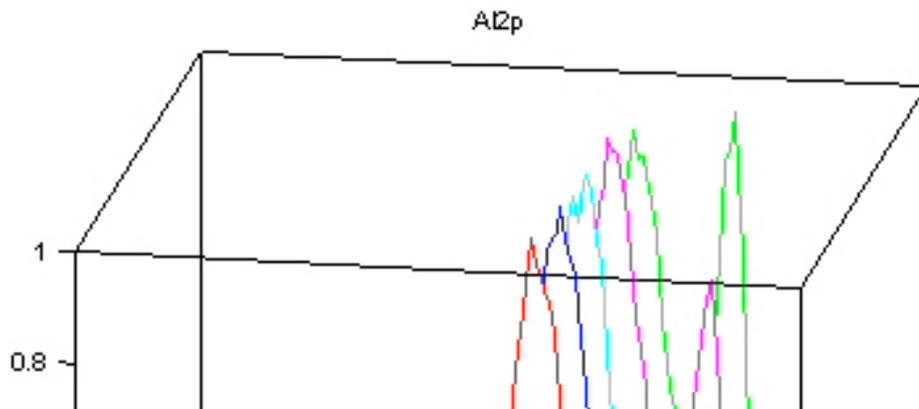
Figure 3 XPS depth profile for Al2p for 100 nm thick Al film on glass. The binding energies for Al-Al and Al-O are 73.0 eV and 75.6 eV, respectively. Data is normalized with respect to the Al-O peak.

The O1s peak also undergoes a similar shift as seen in the XPS depth profile shown in Figure 4. The shift to higher energies indicates the presence of a higher oxidation state, perhaps $Al(OH)_3$. This suggests that the oxide layer is a bi-layer structure; composed of $Al(OH)_3$ and on Al_2O_3.
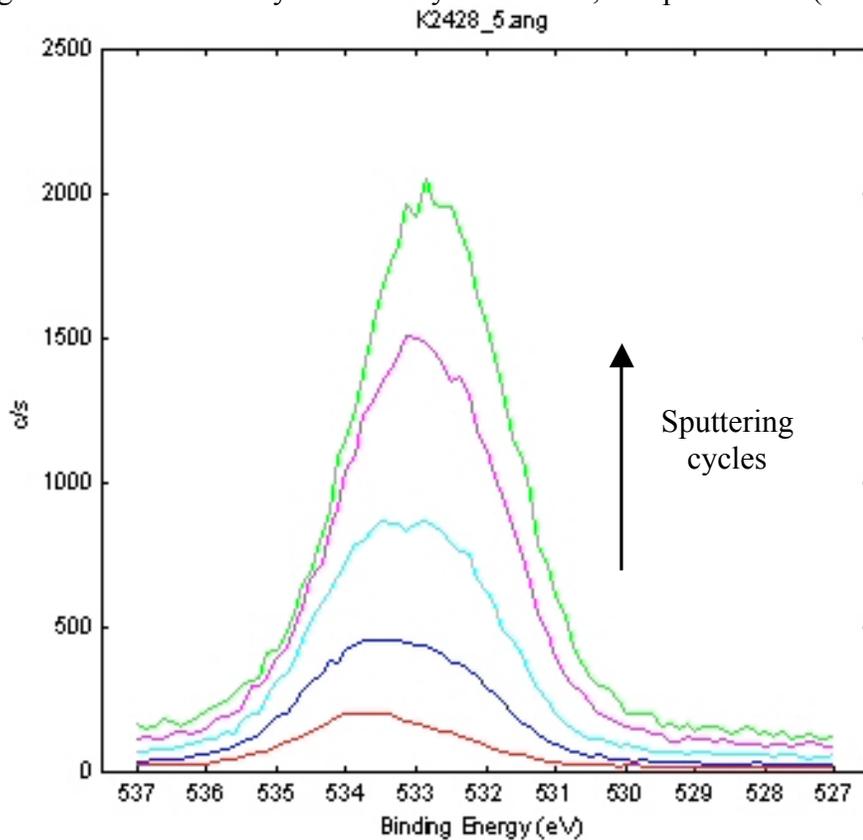
Figure 4 XPS depth profile for O1s showing a shift to a lower energy as the sputtering depth increases. The energies observed are in good agreement with the data from the literature considering the data shown here is not corrected nor normalized.

Auger analysis appears to agree with the XPS results. Figure 5 shows an Auger depth profile of Al films with thicknesses of 100, 250, 500 and 1000 nm. The Al/O ratio on the sample surface changes from 1 to approximately 50 after several sputtering cycles. However this ratio does not show a sharp increase indicating the absence of discrete layers, as also suggested by XPS measurements.

Currently, work in progress is directed at optimizing the growth of Si films at high temperatures, above the Si-Al eutectic. Previously, we have reported that such high temperature Si deposition on Al was problematic since the Al films appear to become discontinuous. Recently, it was

found that Al films heated to 600°C in vacuum remained continuous. Thus the problem may be related to de-wetting of the liquid phase formed at the eutectic. Buffer layers between the glass and Al will be studied to see if they can maintain wetting on the glass hence give continuous Al films with Si film deposition at T>600°C. Additionally, a series of Si films have been deposited by HWCVD on c-Si substrates under conditions, which may lead to epitaxial growth. Samples are being prepared for TEM measurements. These experiments will provide a condition to grow large grain Si films with controlled doping on AIC Si templates.
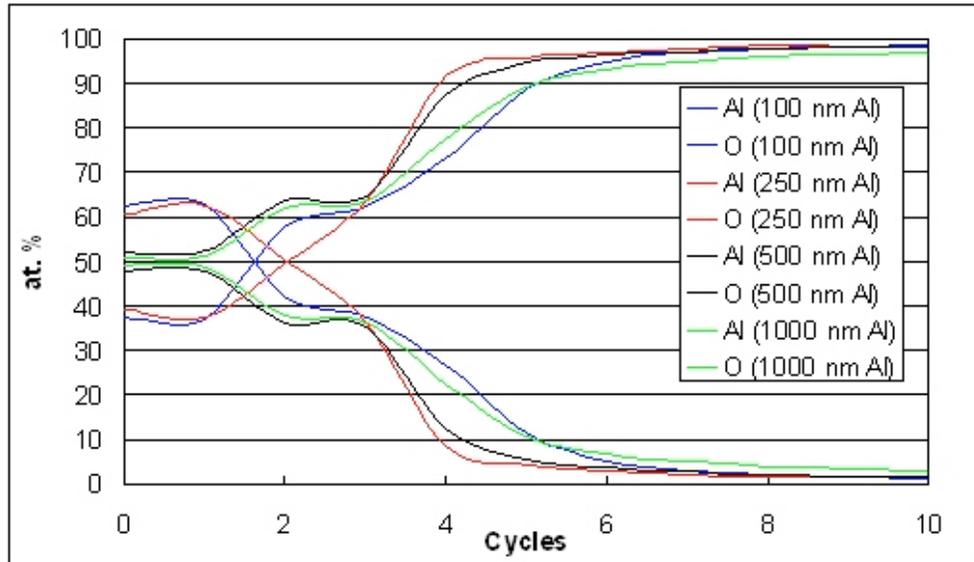
Figure 5 Auger depth profiles showing the change in composition of the aluminum oxide layers.

Task 4 Process diagnostics

A paper describing contact wetting angle measurements to determine surface energy has been prepared for submission to Journal of Vacuum Science and Technology. The abstract of the paper titled "Characterization of CdTe/CdS solar cell surfaces by contacting wetting angle" is given below.

The feasibility of contact wetting angle measurements as a diagnostic tool for evaluating surface energy at different processing stages in thin-film CdTe/CdS solar cell fabrication is evaluated. The polar and dispersive components of surface energy are determined from contact wetting angle measurements conducted using water and formamide. Surface energies are determined for In_2O_3: SnO (ITO), CdS, $Cd_{1-x}Zn_xS$ and CdTe films in as-deposited and treated conditions. Treatments include thermal anneal in air, inert, and $CdCl_2$ ambient as well as surface etching. Differences in surface energies resulting from processing are correlated to changes in surface chemistry and structure detected by utilizing GIXRD, XPS and spectroscopic ellipsometry measurements. For sputtered ITO and chemical surface deposited CdS, an increase in polar surface energy is correlated with recrystallization of the films resulting from the treatments. For chemical surface deposited $Cd_{1-x}Zn_xS$ with x up to 0.4, incorporation of Zn decreases the

dispersive and increases the polar components of surface energy. Native oxidation of the surface of CdTe occurs rapidly (~minutes) and is observable by a reduction of the wetting angle of water and by ellipsometry. Comparison of single crystal (Cd and Te face) films exposed to air and $CdCl_2$ treated films exhibit similar surface energy components. The addition or removal of oxides to CdTe through processing is detected by changes in the polar energy of the treated surface.

References

[1] O. Nast and A. J. Hartmann, J. Appl. Phys. 88, 716 (2000)

Sincerely,

Robert W. Birkmire
Director

RWB/bj
Cc: Paula Newton
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