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Buffer-layer Effect on Mixed-Phase Cells Studied by Micro-Raman and Photoluminescence Spectroscopy

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ABSTRACT

We use micro-Raman and photoluminescence (PL) spectroscopy to study the effects of an a-Si:H buffer layer at the *i/p* interface of the mixed-phase silicon solar cells. We find that the signature of the crystalline 520 cm^{-1} mode still appears on the Raman spectrum for the cells with a 100 Å thick a-Si:H buffer layer; but it completely disappears for cells with a 500 Å thick a-Si:H buffer layer. At 80 K, the PL spectral lineshape reflects the features of the electronic states in the band tails. The characteristics of the PL spectra of the mixed-phase cells are a narrower main band than the standard a-Si:H band and an extra low energy band from the grain boundary region. As the thickness of the a-Si:H buffer layer increases, the PL main band becomes broader, and the low energy band is depressed. We find that, after light soaking, the PL main band is slightly broadened for the cells with no a-Si:H buffer layer, almost no change for the cells with a 100 Å thick buffer layer, and a remarkable decrease in total PL intensity for the cells with a 500 Å thick buffer layer. In addition, the PL intensity of the defect band increases after light soaking for the cells with a 500 Å thick buffer layer, where light-induced defect generation in the a-Si:H buffer layer masks the changes in the mixed-phase intrinsic layer. The Raman and PL results are consistent with previous observations of the effect of an a-Si:H buffer layer on the performance and metastability against light soaking for mixed-phase solar cells.

INTRODUCTION

A light induced open-circuit voltage (V_{oc}) increase has been observed in mixed-phase hydrogenated silicon solar cells, where the intrinsic layer contains a small amount of nanocrystalline grains in the amorphous matrix [1-2]. An increase of photoluminescence (PL) intensity and a blue shift of the peak energy at 80 K have been observed previously in an *in-situ* light soaking experiment. The V_{oc} increase was initially explained by light-induced structural changes, i.e. an expansion of the amorphous phase and a reduction of the crystalline phase [1-2]. However, the structural change model [3] explains the light-induced enhancement of volume on the order of 0.1-0.01%, while the observed V_{oc} increase is as large or greater than 15%. Both x-ray diffraction (XRD) and Raman did not find any observable light-induced structural changes in the mixed-phase materials [4]. Meanwhile, micro-Raman found non-uniform distribution of the nanocrystalline grains on a micrometer-scale in the mixed-phase cell [5]. Experimental results also showed [4] that the V_{oc} enhancement can be suppressed by applying a reverse bias during light soaking, which suggested that the effect is driven by the recombination of photo-generated carriers, the same as the usual Staebler-Wronski effect [6]. Furthermore, when a fully amorphous silicon buffer layer (~ 500 Å) was inserted between the mixed-phase intrinsic and the *p* layers, the solar cells showed high initial V_{oc} and no light-induced enhancement in V_{oc}. Based on those observations, we have proposed a two-diode equivalent-circuit model [4], which explains most of the experimental results. A mixed-phase cell was considered as two diodes connected in parallel: one cell with an amorphous signature of V_{oc} ~1.0 V and the other with a microcrystalline signature of V_{oc} ~0.5 V. The lateral transport between the two cells is negligible. According to the experimental I-V characteristics for good and poor quality µc-Si cells, the V_{oc} increase in a mixed-phase cell can be understood as the metastable defect creation in both µc-Si:H and a-Si:H diodes [4,7]. Indeed, the increase of V_{oc} is always accompanied with degradation of the fill factor (FF) and short circuit current density (J_{sc}). A thin a-Si:H (100 Å) buffer layer did not change the light-induced V_{oc} increase, which was explained by carrier tunneling through the thin buffer layer. However, a thick (500 Å) buffer layer eliminated the light-induced V_{oc} increase, since it blocks the current path through the microcrystalline phase [4,7].

In this paper, we use micro-Raman and PL spectroscopy to further study the effects of an a-Si:H buffer layer on the microstructure and electronic density of states in mixed-phase solar cells.

EXPERIMENTAL AND RESULTS

Mixed-phase silicon *n-i-p* solar cells were deposited using a RF glow discharge on specular stainless steel (ss) substrates. The *i* layer is about 250-nm thick. The top contacts are Indium-Tin-Oxide (ITO) dots with an active area of 0.25 cm^2. The solar cells in the first group were from sample L13869, where differences in the crystalline volume fraction and cell performance are due to a nonuniform deposition [2]. In this sample, no a-Si:H buffer layer was deposited between the mixed-phase intrinsic layer and the doped layers. The cells in the second (sample L13868) and third (sample L13870) groups were deposited under the same conditions as in the first group except an a-Si:H buffer layer with a thickness of 100 Å and 500 Å, respectively, was deposited between the *p* layer and the *i* layer. The initial cell performances are listed in Table I. In the initial state, the 100 Å thick buffer layer blocks the shunt current and increases V_{oc} and FF for the mixed-phase solar cells (cell 11 and cell 13) [8], but does not show an effect on the cell with a fully amorphous signature (cell 23). Increasing the thickness of the buffer layer to 500 Å, the initial V_{oc} is still increased for the mixed-phase cells, but the FF decreases due to a kink in the J-V curve caused by inadequate tunneling through the a-Si:H buffer layer. After light soaking, the light-induced V_{oc} increase was observed in both the cells with no buffer layer and with a 100 Å thick buffer layer, but was not observed in the cells with a 500 Å thick buffer. Details can be found elsewhere [4,7].

Table I. The initial performance of the mixed-phase solar cells with different a-Si:H buffer layers at the *i/p* interface.

Sample #	Cell #	Buffer (Å)	P_{max} (mW/cm^2)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF
L13869	11	0	4.39	10.8	0.695	0.587
	13	0	5.47	10.3	0.852	0.621
	22	0	7.05	10.3	1.001	0.682
L13868	11	100	4.77	10.9	0.725	0.604
	13	100	6.08	10.4	0.905	0.644
	23	100	7.08	10.4	1.003	0.680
L13870	11	500	4.19	11.4	0.911	0.403
	13	500	6.83	11.3	0.970	0.625
	22	500	7.35	11.3	0.979	0.664

Raman measurements were made under ambient conditions directly on these solar cells using the 514.5-nm line from an argon-ion laser. The frequency was calibrated using the transverse optical (TO) mode of a (111) c-Si wafer at 520 cm^{-1}. The penetration depth of the 514.5-nm light is

~ 600 Å for a-Si:H. Therefore, the structure of the top layer, which includes the buffer layer, was measured. Four spots were studied for each cell to evaluate the structural non-uniformity. PL spectra were measured in a temperature range of 80-300 K using a 632.8-nm laser excitation. The penetration depth of the 632.8-nm light is ~1 µm for a-Si:H. Hence, the overall electronic states in the a-Si:H buffer layer and the mixed-phase intrinsic layer are probed.

Figure 1 shows the Raman spectra for the nine cells on the three samples. The three curves from the bottom to top in each plot are arranged with increasing microcrystallinity (decreasing V_{oc}). One can see that the corresponding curves in Fig. 1(b) for the samples with a 100 Å thick a-Si:H buffer layer are almost identical to those in Fig. 1(a) for the samples with no buffer layer. This is because the 514.5-nm laser light penetrates through the 100 Å thick a-Si:H buffer layer, and the signature of the microcrystalline grains still appears on certain areas of the cell. However, no microcrystalline signature is observed on the spectra of the sample with a 500 Å thick a-Si:H buffer layer since the Raman scattering is mainly from the a-Si:H buffer layer. Concerning the relation between the Raman spectrum and V_{oc}, we find that for $V_{oc} \geq 0.911$ V, regardless of the crystallinity and the buffer layer, the TO mode peaked at ~ 480 cm^{-1} with a width of 68 cm^{-1} but without the peak or shoulder at 520 cm^{-1}, indicating a typical amorphous structure. In this case, the crystallinity in the probed region near the *i/p* interface is below the measurement sensitivity.

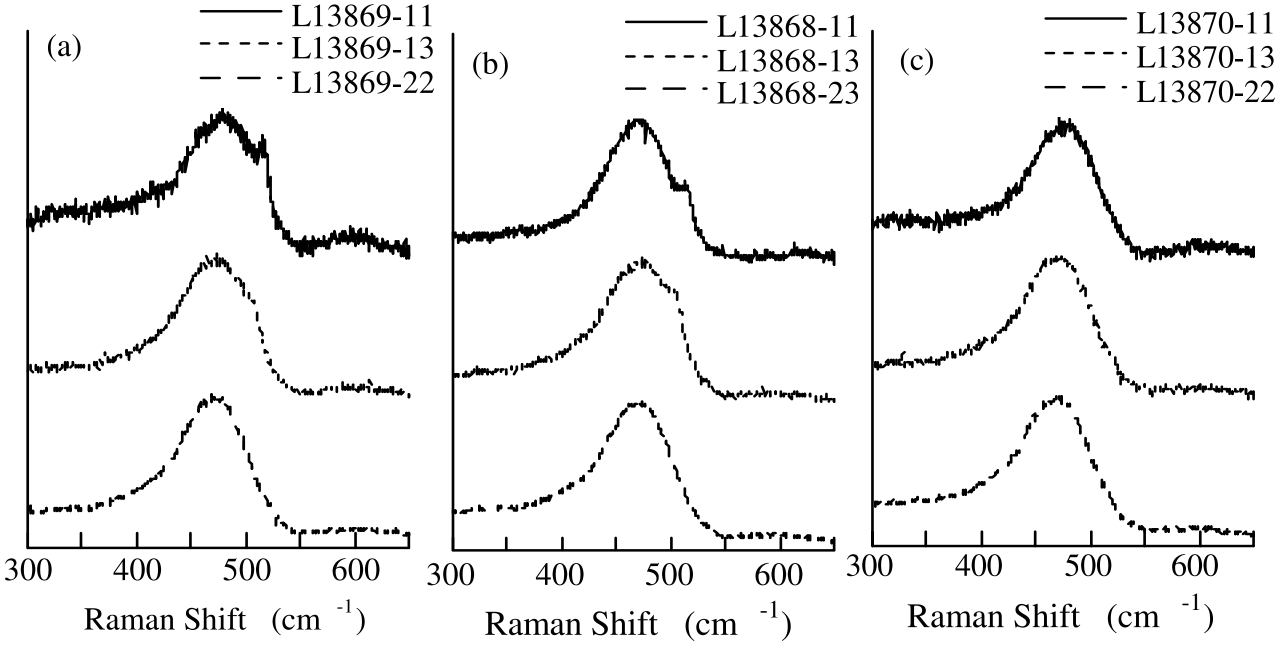

Figure 1. Raman spectra for the cells on (a) L13869, (b) L13868, and (c) L13870, corresponding to no buffer layer, 100 Å thick a-Si:H buffer layer, and 500 Å thick a-Si:H buffer layer, respectively.

We now show the effect of crystallinity in the mixed-phase *i*-layer on the PL lineshape. Figure 2 shows the PL spectra at 80 K for the three cells on sample L13869. As the crystallinity increases,

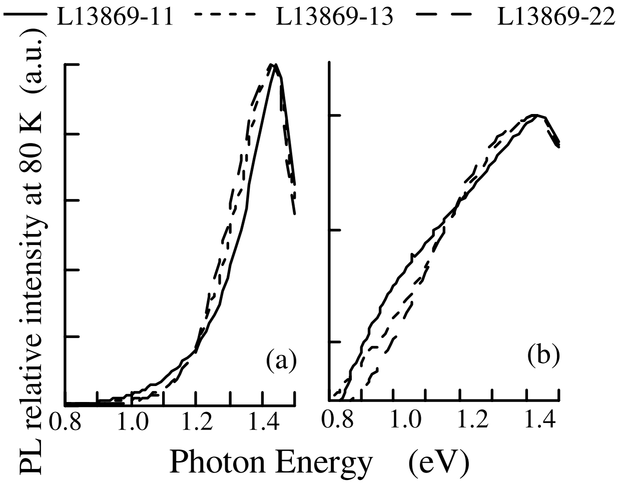

Figure 2. PL spectra at 80 K for cells 11, 13, and 22 on sample 13869 for (a) linear and (b) semi-log plots.

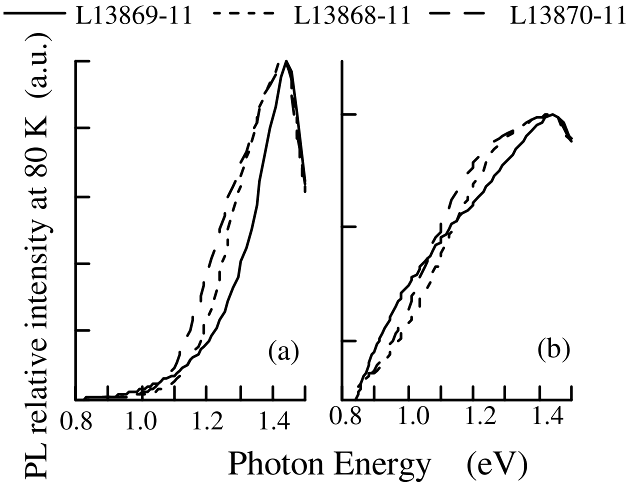

Figure 3. PL spectra of the low V_{oc} cells of L13869-11, L13868-11, and L13870-11 for (a) linear and (b) semi-log plots.

the main band becomes narrower; and the low energy (<1.2 eV) signal increases as seen clearly in the semi-log plot. When a portion of the microcrystalline phase increases, the band tail of the a-Si:H matrix becomes narrower, and extra radiative recombination in the grain boundary (g.b.) region appears [9-11]. We then show the effect of the a-Si:H *i/p* buffer layer on the PL lineshape. Figure 3 plots the PL spectra of cell 11 from the three samples. These cells are located at the same position on the substrate, but with different thickness of the a-Si:H buffer layer (0, 100 Å, and 500Å). The a-Si:H buffer layer makes the PL main band broad, and the low energy PL band from the g.b. regions is suppressed, which is similar to decreasing the crystallinity as shown in Fig. 2. The differences in the PL features among the nine cells can also be seen from the temperature (T) dependence of the PL intensity (I_{PL}). As shown in Fig. 4 for mixed-phase cells, the PL spectrum generally contains three components: a main band from a-Si:H at high energy with a strong temperature dependence (O), a g.b. (Δ) band at low energy with a weak temperature dependence, and a defect band (■) that appears only at T>180 K. For the cells with no a-Si:H buffer layer (sample L13869), with the increase of crystallinity (from cell 22 to 11), the PL intensity of the g.b. band increases, and the slope of the I_{PL}-T plot of the a-Si:H component becomes steeper. By fitting the data to $I_{PL} = I_o \exp(-T/T_L)$, we obtained a PL characteristic temperature of T_L~20 K for cell 11, which is smaller than those from the other two cells (~22 K). A smaller T_L implies a narrower band tail. Therefore, the PL intensity result is consistent with the PL lineshape, where cell 11 has the narrowest bandwidth as shown in Fig. 2. For the cells with a 100 Å thick a-Si:H buffer layer (sample L13868) as shown in Fig. 4 (b), the a-Si:H main-band and defect-band for the three cells are close to each and the g.b. band still appears in the same order as in Fig. 4(a) but with a relatively weak intensity, which is due to the PL contribution from the a-Si:H buffer layer. The spectra in Fig. 4(c) show typical characteristics for intrinsic a-Si:H films. Only the a-Si:H main-band and the defect-band are observed. The g.b. band is completely suppressed due to the PL contribution from the 500 Å thick a-Si:H buffer layer. In addition, the PL spectra for these three cells show the common features of the a-Si:H, including the T_L around 20-

22K, the PL peak energy around 1.40-1.42 eV at 80 K, and the temperature coefficient of the peak energy around 1.5-2.0 meV/K. These data indicate a good quality a-Si:H matrix for the cells.

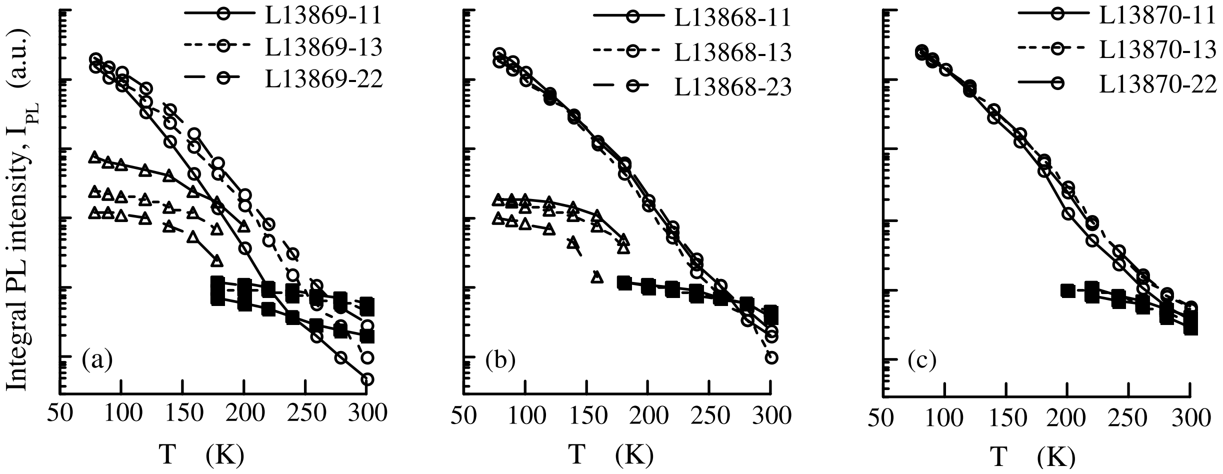

Figure 4. PL intensities vs. temperature for cells of (a) L13869, (b) L13868, and (c) L13870, where circles represent the a-Si:H main band, triangles the g.b. band, and squares the defect band.

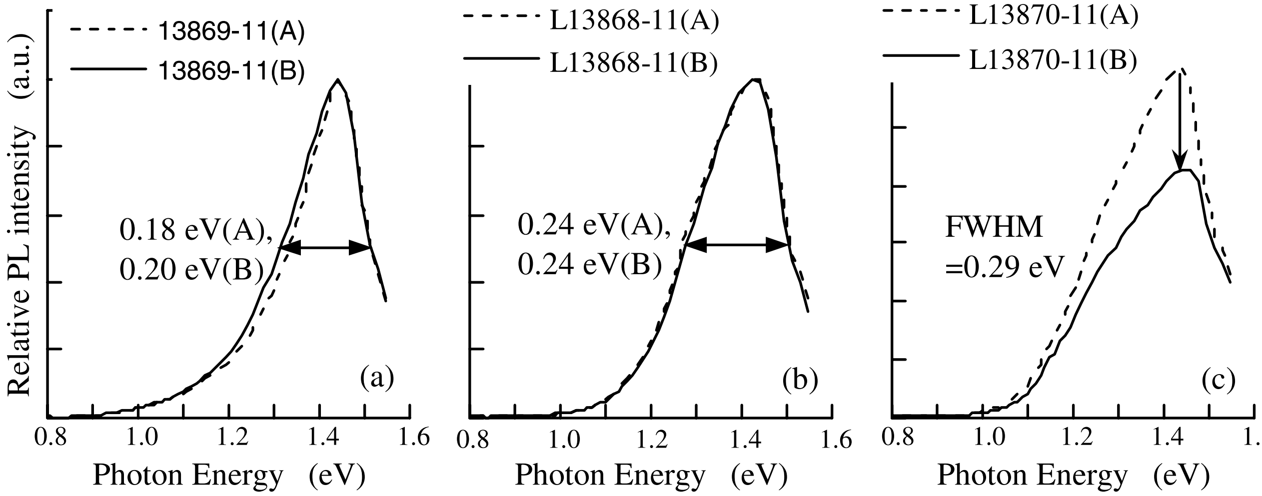

Figure 5. PL spectra at 80 K before and after light soaking for cells of (a) L13869-11, (b) L13868-11, and (c) L13870-11.

After the PL was measured in the initial state (state A), *in-situ* light soaking was done at room temperature for 4 hours using a 200 mW/cm^2 white light with an infrared cut-off filter. The PL spectrum was then measured at temperatures from 80 K to 300 K in the light soaked state (state B). Correlated with V_{oc} increase an increase of PL intensity at 80 K have been observed in an *in-situ* light soaking experiments in mixed-phase solar cells [2]. It was explained by light-induced structural changes, i.e. an expansion of the amorphous phase and a reduction of the crystalline phase [2]. Figure 5 shows the PL spectra at 80 K before and after light soaking for cells L13869-11, L13868-11, and L13870-11. For the cell without a-Si:H buffer layer, we find that the PL main band becomes slightly wider and the PL total intensity also increases slightly in Fig. 5(a), consistent with our previous observation [2]. For cell L13868-11 in Fig. 5(b), no detectable change is found on the PL spectra, which could be due to the opposite effect of the thin a-Si:H buffer layer (PL intensity decreases upon light soaking) and mixed-phase intrinsic layer (PL intensity increases upon light soaking) on PL. When the a-Si:H buffer layer was as thick as 500 Å, the light soaking effects in the buffer layer dominate. The cell L13870-11 in Fig. 5(c) shows a large change in both the lineshape and intensity. The total PL intensity is decreased by ~40% and the relative intensity of the defect band increases, which is normally observed in a-Si:H.

SUMMARY

Similar features in both the Raman and PL spectra were observed in the mixed-phase cells with 0 and 100 Å thick a-Si:H buffer layers at the *i/p* interface. Both the Raman and PL results were similar to standard a-Si:H solar cells when the a-Si:H buffer layer is 500 Å thick, where the crystalline silicon TO mode on the Raman spectra and the g.b. component on the PL spectra completely disappear. In the initial state, a thick a-Si:H buffer layer results in a broader PL spectrum and a suppression of the g.b. PL band, which correlates to a higher initial V_{oc}. Light soaking results in a slight broadening in the PL main band for the mixed-phase cell with no a-Si:H buffer layer. The light-induced defect generation in the 500 Å thick a-Si:H buffer layer masked the changes in the mixed-phase intrinsic layer underneath. The Raman and PL results are consistent with the solar cell results in the sense that a thin (100 Å) a-Si:H buffer layer does not change the behavior of the mixed-phase solar cells upon light soaking, but a thick (500 Å) buffer layer does.

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