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Surface passivation of Cu(In,Ga)Se₂ using atomic layer deposited Al₂O₃

W.-W. Hsu,¹ J. Y. Chen,¹ T.-H. Cheng,² S. C. Lu,² W.-S. Ho,¹ Y.-Y. Chen,¹ Y.-J. Chien,³ and C. W. Liu^{4,a)}

¹Graduate Institute of Electronics Engineering and Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan

²Graduate Institute of Photonics and Optoelectronics and Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan

³Advanced Technology Department, TF RD & System Dev. Div. AU Optronics Corporation, Taichung, Taiwan ⁴Graduate Institute of Electronics Engineering, Graduate Institute of Photonics and Optoelectronics, Department of Electrical Engineering, Center for Condensed Matter Sciences, and Center for Emerging Material and Advanced Devices, National Taiwan University, Taipei, Taiwan and National Nano Device Laboratories, Hsinchu, Taiwan

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With Al₂O₃ passivation on the surface of Cu(In,Ga)Se₂, the integrated photoluminescence intensity can achieve two orders of magnitude enhancement due to the reduction of surface recombination velocity. The photoluminescence intensity increases with increasing Al₂O₃ thickness from 5 nm to 50 nm. The capacitance-voltage measurement indicates negative fixed charges in the film. Based on the first principles calculations, the deposition of Al₂O₃ can only reduce about 35% of interface defect density as compared to the unpassivated Cu(In,Ga)Se₂. Therefore, the passivation effect is mainly caused by field effect where the surface carrier concentration is reduced by Coulomb repulsion. © 2012 American Institute of Physics. [doi:10.1063/1.3675849]

The Cu(In,Ga)Se₂ (CIGS) thin film solar cell has a potential to reduce production cost for photovoltaic modules. The record efficiency of the CIGS thin film solar cells is ~20%.¹ To solve the additional surface recombination at the edge of the damage area by laser scribing,^{2,3} a good passivation layer for CIGS is necessary. In this letter, atomic layer deposited (ALD) Al₂O₃ is investigated to passivate the CIGS, and the effect of the passivation is measured by photoluminescence (PL). The effectiveness of passivation is due to both the low interface defect density (Q_{it}) at the CIGS/Al₂O₃ interface and the negative fixed charges (Q_f) in bulk Al₂O₃ for field effect passivation.

CIGS films with a thickness of $\sim 2 \ \mu m$ were deposited on $\sim 1 \ \mu m$ Mo on glass by coevaporation at 500 °C. The Al₂O₃ layers were deposited by the ALD at 250 °C, lower than the CIGS deposition temperature. The alternating pulses of trimethyl aluminum (Al(CH₃)₃, TMA) and H₂O in an Ar carrier gas were used to deposit the Al₂O₃ layers. Each cycle includes TMA for 0.03 s, Ar purge for 10 s, H₂O for 0.06 s, and Ar purge for 10 s. The thickness of the deposited Al_2O_3 film was determined by the number of ALD cycles. The chamber of the Al₂O₃ deposition is different from the chamber of the CIGS deposition. During the transportation, a vacuum bag is used to minimize the exposure in air. The PL spectra of the same sample were measured before and after the Al₂O₃ deposition by the lock-in technique with the laser excitation wavelength of 671 nm and the pumping power of 100 mW. Note that the Al₂O₃-deposited CIGS has longer air exposure time than the as-grown CIGS.

Figure 1 shows the PL spectra at room temperature of the coevaporated CIGS film with and without Al_2O_3 (50 nm) passivation, where the PL signal of the unpassivated sample

is multiplied by a factor of 100. The PL emission shoulder at 1.15 eV is due to the band-impurity (BI) recombination between electrons in the conduction band and holes at acceptor levels⁴ (the inset of Fig. 1). The emission peak at 1.09 eV is due to the recombination from donor-to-accepter pair (DAP) between donor levels and acceptor levels.^{4,5} The Al₂O₃ passivated CIGS have 200 times integrated PL intensity of the unpassivated CIGS due to the low effective surface recombination velocity (S_{eff}). Al₂O₃ can serve as a good passivation layer for CIGS films.

The correlation between the S_{eff} and the PL intensity is simulated using 50 ns and 250 ns lifetime of bulk CIGS, which covers typical reported lifetime of CIGS films (Fig. 2).^{6–8} The electron and hole concentration profiles of the CIGS films are simulated under one sun illumination



FIG. 1. (Color online) PL spectra of coevaporated CIGS films with and without 50 nm thick Al_2O_3 passivation at room temperature. The Al_2O_3 passivated CIGS has 200 times integrated PL intensity of the unpassivated CIGS. The inset shows the recombination mechanisms.

^{a)}Author to whom correspondence should be addressed. Electronic mail: chee@cc.ee.ntu.edu.tw.



FIG. 2. (Color online) Simulated S_{eff} and the PL intensity using 50 and 250 ns lifetime of bulk CIGS. Each curve is normalized with respect to the S_{eff} of the unpassivated surface, which is assumed to be 1×10^6 cm/s.

(100 mW/cm², AM 1.5 G), and the radiative recombination is proportional to the product of the electron and hole concentrations.⁸ The parameter used in the simulation such as refractive index, extinction coefficient, mobility, effective density of state (DOS), and dielectric constant are adapted from Refs. 9 and 10. Each curve is normalized with respect to the S_{eff} of the unpassivated surface, which is assumed to be 1×10^6 cm/s.^{8,11} At S_{eff} larger than 10^4 cm/s, the PL intensity is independent on life time (τ_b), while the dependence is stronger for S_{eff} smaller than 10^4 cm/s. With the deposition of 50 nm thickness Al₂O₃, the PL intensity enhances by 200 times as compared to the unpassivated surface. Our calculation indicates the S_{eff} is reduced to 14 to 44 cm/s for 50 nm Al₂O₃ passivation using $\tau_b = 50$ ns to 250 ns.

To have a clear picture of interface defect density (D_{it}) and field effect on Al₂O₃ passivation, the DOS is calculated using first principal calculation. Al₂O₃ has a variety of phases, but is amorphous in Al₂O₃/CIGS structure. Simulation of amorphous phases using finite supercells is difficult due to the uncertainty of structures and the lack of longrange order.¹² For simplicity, we have chosen κ -phase Al₂O₃ with the most representative density of the amorphous oxide¹³ (Fig. 3(a)) in our calculation. Fig. 3(b) shows the simulated DOS at the surface layer of the CIGS for unpassivated CIGS and the Al₂O₃ passivated CIGS. Al₂O₃ passivation can reduce about 35% of the D_{it} as compared to unpassivated surface. Considering the reduction of the D_{it} effect only, the S_{eff} can be only reduced about 35% approximately, which is not sufficient to explain the experimental enhancement.

Al₂O₃ is well-known to have excess defects with negative fixed charges in oxygen-rich condition, while to have excess defects with positive fixed charges in aluminum-rich condition.¹² As shown in the inset of Fig. 4, a positive flat band shift of the capacitance-voltage curve from a 10 nm Al₂O₃ device to a 50 nm Al₂O₃ device is observed, indicating negative fixed charge in bulk Al₂O₃. In Figure 4, the correlation between S_{eff} and Q_f with D_{it} = 2×10^{12} and D_{it} = 4×10^{12} cm⁻² is simulated. The energy distribution of interface trap density, electron capture cross section σ_n , and hole capture cross section σ_p are taken from Refs. 14 and 15. The recombination rate (U_s) is obtained by an integration over the band gap,

$$U_{s} = (n_{s}p_{s} - n_{i}^{2})v_{th} \\ \times \int_{E_{v}}^{E_{c}} \frac{D_{it}(E_{t})}{(n_{s} + n_{1})/\sigma_{p}(E_{t}) + (p_{s} + p_{1})/\sigma_{n}(E_{t})} dE_{t}.$$
 (1)

The definition of each term in Eq. (1) is referred to Ref. 16. S_{eff} is then determined by $U_s/\Delta n$, where Δn is the light generated excess minority concentration. S_{eff} decreases with increasing fixed charge density for both negative charge and positive charge. With negative fixed charge smaller than 1×10^{12} cm⁻², the field effect passivation is not effective, while the dependence is stronger for negative fixed charge larger than 1×10^{12} cm⁻². Since σ_p of 6×10^{-18} cm² is smaller than σ_n of 5×10^{-16} cm², the S_{eff} at positive Q_f is smaller than that at negative of 50 nm Al₂O₃ on CIGS is larger than 3×10^{12} cm⁻² to have S_{eff} = 14 to 44 cm/s (Fig. 4). The negative fixed charge is consistent with the case of



FIG. 3. (Color online) (a) The structure used in the first principle calculation. (b) The calculated density of states of the unpassivated CIGS and the Al₂O₃/CIGS interface. The D_{it} of passivated CIGS is 35% lower than the surface state density of the unpassivated CIGS.

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FIG. 4. (Color online) The simulated S_{eff} as a function of fixed charge. S_{eff} decreases with the increasing fixed charge density for both negative charge and positive charge. The inset shows the capacitance voltage measurement of CIGS with Al₂O₃ thickness of 10 nm and 50 nm.

 Al_2O_3 deposited on Si.¹² Note the incremental fixed charge density from 10 nm Al_2O_3 to 50 nm Al_2O_3 is about 1×10^{12} cm⁻² from the CV measurement.

Fig. 5 shows the integrated PL intensity for different thickness of Al_2O_3 and annealing time with nitrogen and forming gas. The integrated PL intensity increases with increasing thickness of Al_2O_3 , indicating the larger density of fixed charge in thicker Al_2O_3 has better passivation. The effects of thermal budget (250 °C, 34 min–168 min) in N_2 and forming gas are also investigated. The PL intensity after N_2 and forming gas annealing with the same thermal budget has the same intensity as the unpassivated CIGS. Therefore, the Al_2O_3 is the root of cause responsible for the surface passivation.

Surface passivation of CIGS using ALD Al_2O_3 is demonstrated for the first time. Even with the thickness of only 5 nm, the passivation effect is still observable. The effectiveness of passivation is mainly due to the negative fixed charges in bulk Al_2O_3 for field effect passivation. Al_2O_3 can be used for the edge passivation of CIGS module after p3 scribing to reduce the surface recombination velocity at edge. This can increase the shunt resistance, short circuit current, and open circuit voltage of the cell based on our simulation.



FIG. 5. (Color online) The integrated PL intensity as a function of Al_2O_3 thickness and annealing time. The PL intensity after N_2 and forming gas annealing is the same as the original CIGS.

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