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MODELING Cu MIGRATION IN CdTe SOLAR CELLS UNDER DEVICE-PROCESSING AND LONG-TERM STABILITY CONDITIONS

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Abstract

An impurity migration model for systems with material interfaces is applied to Cu migration in CdTe solar cells. In the model, diffusion fluxes are calculated from the Cu chemical potential gradient. Inputs to the model include Cu diffusivities, solubilities, and segregation enthalpies in CdTe, CdS and contact materials. The model yields transient and equilibrium Cu distributions in CdTe devices during device processing and under field-deployed conditions. Preliminary results for Cu migration in CdTe PV devices using available diffusivity and solubility data from the literature show that Cu segregates in the CdS, a phenomenon that is commonly observed in devices after back-contact processing and/or stress conditions.

Diffusion-Segregation Model: Pseudo-Binary Diffusion Couple Formulation

Free Energy

$$A = \sum_i \left[\left(n_i X^i_{Cu} \right) \mu^i_{Cu} + \left(n_i X^i_p \right) \mu^i_p \right]$$

Chemical Potential

$$\mu^i_{\text{Cu-}p} = \frac{1}{n_i} \frac{\partial A}{\partial X^i_{\text{Cu}}} = \Delta H^i_{\text{Cu-}p} + kT \ln \frac{X^i_{\text{Cu}}}{1 - X^i_{\text{Cu}}}$$

Migration Potential

$$\Delta H^i_{\text{Cu-}p} = -\left(E^i_D + \phi^i_{\text{Cu-}p} \right)$$

Segregation Enthalpy

$$H_{\text{seg}} = \Delta H_{\text{Cu-}p} - \Delta H_{\text{Cu-}p'}$$

POhenomenological Flux Eq.

$$J_{\text{Cu}} = -M C_{\text{Cu}} \frac{\partial \mu_{\text{Cu-}p}}{\partial x}$$

Mobility

$$M = \frac{D}{kT} \frac{C_p}{C_0}$$

Migration Flux

$$J = \frac{C_p}{C_0} \left(\frac{DC}{kT} \frac{\partial \phi_{\text{Cu-}p}}{\partial x} - C \frac{\partial D}{\partial x} \right) - D \left(\frac{\partial C}{\partial x} - \frac{C}{C_0} \frac{\partial C_0}{\partial x} \right)$$

Continuity Equation

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}$$

Fick's 1st Law

$$J = -D\left(\partial C / \partial x \right)$$

Migration Potential Near a Pseudo-Binary Diffusion Couple Interface

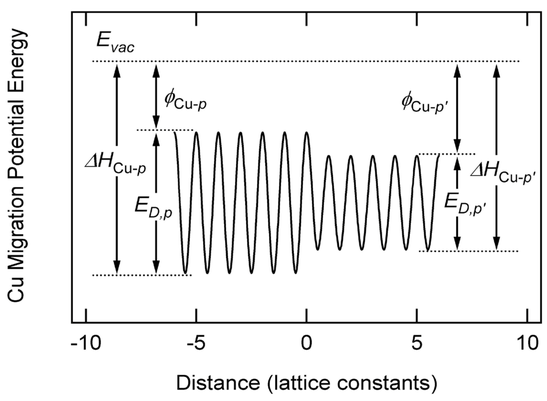

Figure 1. Schematic illustration of the ideal-solution Cu migration potential near a hypothetical material interface.

Device-Processing Simulation Results: High-Diffusivity Case

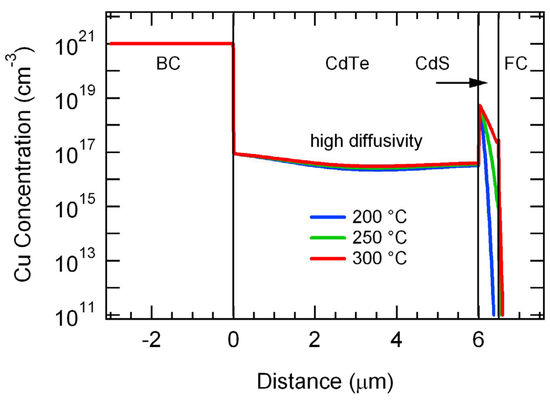

Figure 2. Device-processing simulation of Cu migration in CdTe PV device for the high-diffusivity case.

Device-Processing Simulation Results: Low-Diffusivity Case

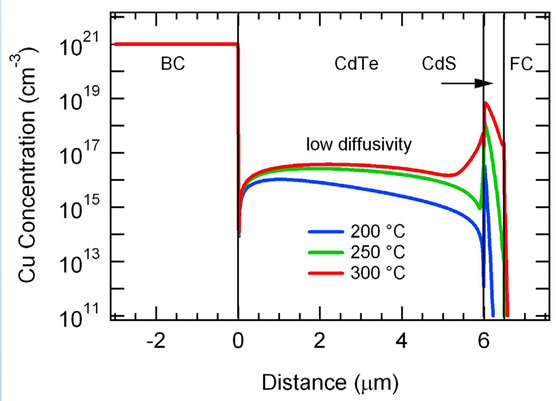

Figure 3. Device-processing simulation of Cu migration in CdTe PV device for the low-diffusivity case.

Survey of Cu Diffusivities and Solubilities in CdTe and CdS

CdTe:Cu diffusivity data				
D_0 (cm^2 s^{-1})	E_D (eV)	Ref.	SC or PX	Diffusion mode
1.70E-06	0.24	[1]		
6.65E-05	**0.57**	**[2]**	SC	low
7.30E-07	0.33	[3]		
1.30E-06	**0.29**	**[4]**	PX	high
8.20E-08	0.64	[5]		
3.70E-04	0.67	[6]		
9.57E-04	0.7	[7]		
CdTe:Cu solubility data				
C_0 (cm^{-3})	E_a (eV)	Ref.		
1.56E+23	**0.55**	**[2]**	SC	low
~2E+17	**~0**	**[4]**	PX	high
3.73E+24	0.68	[8]		
CdS:Cu diffusivity data				
D_0 (cm^2 s^{-1})	E_D (eV)	Ref.		
1.20E-02	1.05	[9]	SC	
2.10E-03	0.96	[10]	SC	
1.60E-03	0.77	[11]	SC	
—	0.95	[12]	SC	
6.00E-09	**0.5**	**[13]**	PX	
—	1.0	[14]	SC	
CdS:Cu solubility data				
C_0 (cm^{-3})	E_a (eV)	Ref.		
8.00E+21	**0.27**	**[13]**	PX	
6.60E+22	0.505	[10]	SC	

Long-Term Stability Simulation Results: High-Diffusivity Case

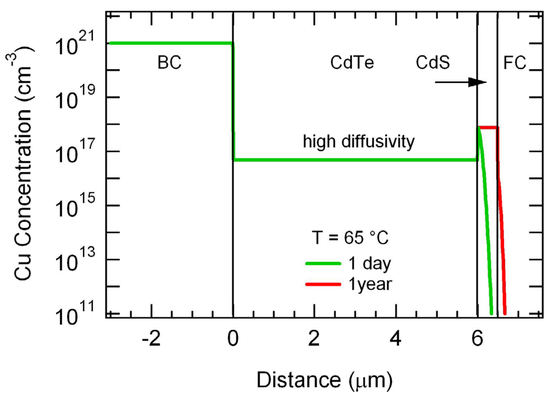

Figure 4. Long-term stability simulation of Cu migration in CdTe PV device for the high-diffusivity case.

Long-Term Stability Simulation Results: Low-Diffusivity Case

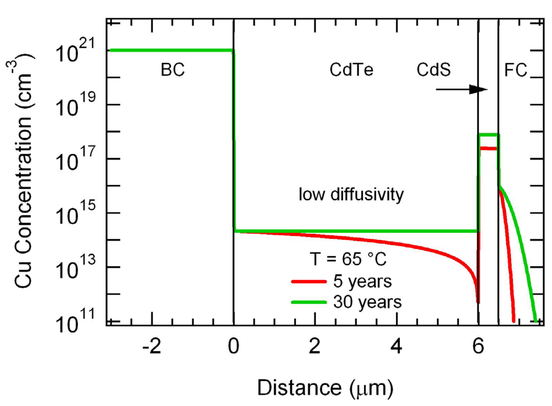

Figure 5. Long-term stability simulation of Cu migration in CdTe PV device for the low-diffusivity case.

SIMS Depth Profile

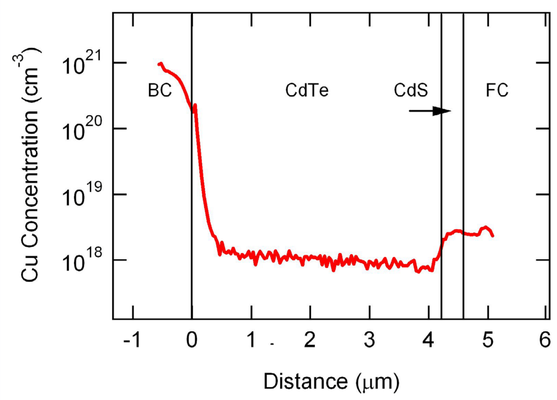

Figure 6. Typical SIMS profile of a ZnTe:Cu back-contacted device after back-contact processing.

REFERENCES

[1] B. O. Wartlick, C. Blanchard, and J. F. Barbot, "Study of silver and copper diffusion in p-type Hg/sub 0.3/Cd sub 0.7/Te and CdTe by capacitance measurements," *Materials Science & Engineering B (Solid-State Materials for Advanced Technology)*, vol. **B71**, pp. 254-257, 2000.
[2] E. D. Jones, N. M. Stewart, and J. B. Mullin, "The diffusion of copper in cadmium telluride," *Journal of Crystal Growth*, vol. **117**, pp. 244-248, 1992.
[3] T. D. Dzhafarov, S. S. Yesilkaya, N. Y. Canli, and M. Caliskan, "Diffusion and influence of Cu on properties of CdTe thin films and CdTe/CdS cells," *Solar Energy Materials and Solar Cells*, vol. **85**, pp. 371-383, 2005.
[4] R. A. Enzenroth, K. L. Barth, and W. S. Sampath, "Transient ion drift measurements of polycrystalline CdTe PV devices," *Conference Record of the 2006 IEEE 4th World Conference on Photovoltaic Energy Conversion (IEEE Cat. No. 06CH37747)*, pp. 4 -4, 2006.
[5] H. Mann, G. Linker, and O. Meyer, "Diffusion processes at the Cu-CdTe interface for evaporated and chemically plated Cu layers," *Solid State Communications*, vol. **11**, pp. 475-479, 1972.
[6] H. H. Woodbury and M. Aven, "Some Diffusion and Solubility Measurments of Cu in CdTe," *Journal of Applied Physics*, vol. **39**, pp. 5485-5488, 1968.
[7] O. E. Panchuk, V. I. Grytsiv, and D. P. Belotskii, "Diffusion of Cu in CdTe," *Inorganic Materials*, vol. **11**, pp. 1510-1512, 1975.
[8] A. V. Vishnyakov, V. N. Zubkovskaya, and T. V. Kukleva, "Solubility of copper in cadmium telluride," *Inorganic Materials*, vol. **25**, pp. 502-505, 1989.
[9] J. L. Sullivan, "An ultrasonic investigation of the diffusion of noble metals in CdS," *Journal of Physics D (Applied Physics)*, vol. **6**, pp. 552-559, 1973.
[10] J. L. Sullivan, "Diffusion and Solubility of Cu in CdS Single Crystals," *Physical Review*, vol. **184**, pp. 796-805, 1969.
[11] R. L. Clarke, "Diffusion of Copper Cadmium Sulfide Crystals," *Journal of Applied Physics*, vol. **30**, pp. 957-960, 1959.
[12] L. V. Borkovskaya, B. R. Dzhumaev, L. Y. Khomenkova, N. E. Korsunskaya, I. V. Markevich, and M. K. Sheinkman, "About the nature of diffusion anisotropy in CdS crystals," *Semiconductor Physics Quantum Electronics & Optoelectronics*, vol. **3**, pp. 282-286, 2000.
[13] E. B. Kaganovich, I. K. Ostrovskaya, Y. S. Pilipyuk, and E. M. Pochtar, "Diffusion and solubility of copper in photoconductive CdS films precipitated from aqueous solution," *Inorganic Materials*, vol. **24**, pp. 1236-1238, 1988.
[14] L. V. Borkovska, L. Y. Khomenkova, N. E. Korsunska, I. V. Markevich, and M. K. Sheinkman, "Some peculiarities of impurity diffusion in CdS crystals," *Physica Status Solidi B*, vol. **229**, pp. 269-273, 2002.

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