

# Rapid Preparation and Photoelectrochemical Screening of CuInSe<sub>2</sub> and CuInMSe<sub>2</sub> Arrays by Scanning Electrochemical Microscopy

Guanjie Liu<sup>†</sup> and Allen J. Bard\*

Center for Electrochemistry, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, United States

Received: June 25, 2010; Revised Manuscript Received: September 9, 2010

CuInSe<sub>2</sub> and CuInMSe<sub>2</sub> (M = Ga, Zn, Cd) arrays were prepared from precursor aqueous:glycerol (3:1) solutions with a robotic piezoelectric dispenser on fluorine-doped tin oxide (FTO) conductive glass. Studies of the photoresponse of spots on the array by scanning electrochemical microscopy (SECM) with an optical fiber tip showed that different annealing temperatures affected the position on the array of the optimal spot (the spot that showed the highest photocurrent). Depositing a thin layer of CdS on the CIS-250 array improved the photoactivity of the spots and also affected the optimal spot position. Adding 20–40% Ga into the CIS array increased the photocurrent, but addition of Zn or Cd did not.

## 1. Introduction

Semiconductor materials have been widely investigated as the absorption layer for photovoltaic (PV) solar cells. Among these materials, p-type CuInSe<sub>2</sub> (CIS) is considered a promising photovoltaic material because of its high efficiency and good photostability. When Ga is added to CIS to form a CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> (CIGS) alloy the efficiency can reach 19.9%.<sup>1</sup> These high-quality absorption layers are usually deposited by vacuum-based methods such as evaporation<sup>1</sup> and sputtering.<sup>2</sup> Recently, a high-quality CIS solar cell with a 12% efficiency was prepared by a novel hydrazine solution process.<sup>3</sup> In addition to being used as an absorber in a solid-state PV cell, CIS and CIGS can also be used as a photoelectrochemical (PEC) photocathode material, e.g., for water splitting with an external bias, as shown recently by the Domen group.<sup>4</sup> In their study, an incident photon-to-current conversion efficiency (IPCE) of 59% was realized for a Pt/CdS/CIGS photocathode. The electrode also showed a high resistance to the reductive decomposition that is often seen with p-type materials in PEC studies.

Combinatorial methods based on automated synthesis and screening provides a rapid and systematic method for developing new photocatalysts. These have been applied, for example, in the search for phosphors, sensors, and fuel cell catalysts.<sup>5,6</sup> Several groups have also employed combinatorial methods for searching the multielement space for photocatalysts.<sup>7–9</sup> Our previous studies have shown the advantage of SECM in the development of new oxide photocatalyst materials.<sup>10–12</sup> Compared with the preparation of oxide samples, an additional soluble selenium source needs to be added into the spots during the preparation of selenide samples. Dimethylselenourea can be used as the selenium source where its dissociation, shown in eq 1, produces H<sub>2</sub>Se, which further dissociates into Se<sup>2-</sup> during the heating process.<sup>13</sup>



Hydrazine in the dimethylselenourea solution provides an oxygen-free condition, allowing the preparation process of the arrays to be carried out under atmospheric conditions.<sup>14</sup> This approach was previously used with SECM screening for the preparation of Zn–Cd–S–Se materials.<sup>15</sup> We extend this approach here with other nonoxide catalysts, where we describe the rapid preparation of CIS and CIMS (M = Ga, Zn, Cd) spot arrays and investigate their photoelectrochemical properties using SECM.

## 2. Experimental Section

**Chemicals.** CuCl<sub>2</sub>, InCl<sub>3</sub>, Ga(NO<sub>3</sub>)<sub>3</sub>, dimethylselenourea, hydrazine, Na<sub>2</sub>SO<sub>4</sub>, and glycerol were used as received, and Milli-Q water was used to prepare all solutions. All precursor solutions were made with a 3:1 (volume) solution of water/glycerol to adjust the volatility, with a single metal salt concentration of 0.1 M, and a concentration of dimethylselenourea solution (containing 0.05 M hydrazine) of 0.15 M.

**Preparation of Photocatalyst Arrays.** The CH Instruments model 1550 dispenser (Austin, TX) used to fabricate the photocatalyst arrays consists of a stepper-motor-operated XYZ stage with a piezodispenser (MicroJet AB-01-60, MicroFab, Plano, TX) attached to the head. The system was connected and controlled through a PC computer. The fluorine-doped tin oxide (FTO) substrate was placed under the piezodispenser tip, and the XYZ stage moved the dispenser head in a preprogrammed pattern, while programmed voltage pulses were applied to the dispenser to eject the requested number of drops (~100 pL each) of the metal precursor solution onto the substrate. The first component (metal precursor solution) was loaded and dispensed in a preprogrammed pattern onto the FTO substrate. After flushing and washing the piezodispenser, the second component was loaded into the dispenser and dispensed into the existing pattern. The step was repeated when a third component was added. The relative number of drops of each metal salt component (~10 total) determined the spot composition. In addition, every spot contained 10 drops of dimethylselenourea solution. The samples were then mixed with a Vortex

\* To whom correspondence should be addressed. E-mail: ajbard@mail.utexas.edu.

<sup>†</sup> On leave from the State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, 710049, China.

Genie 2 (Fisher, Pittsburgh, PA). Finally, The arrays were dried at 100 °C overnight and annealed at different temperatures under an argon atmosphere. These samples are denoted as CIS-250, CIS-350, and CIS-450 (the number represents the annealing temperature). The diameter of the spot was roughly 300  $\mu\text{m}$ , and the thickness was about 400 nm. The distance between the center of the spots was 700  $\mu\text{m}$ .

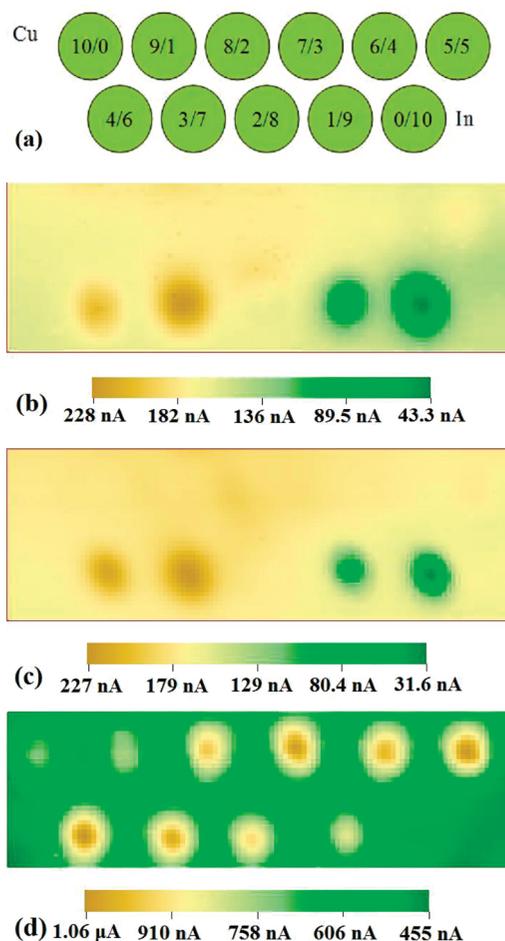
A CdS layer was deposited on some samples using the chemical bath method.<sup>16</sup> The solution consisted of 0.0015 M CdSO<sub>4</sub>, 0.0075 M thiourea, and 1.5 M NH<sub>4</sub>OH. The samples were immersed in the bath at room temperature, and the temperature of the bath was increased to 60 °C for 16 min.

**Screening the Spot Arrays.** A schematic of the SECM setup was shown in a previous paper.<sup>17</sup> An optical fiber (FT-400-URT, 3M, diameter, 400  $\mu\text{m}$ , St. Paul, MN) connected to a 150 W xenon lamp was attached to the tip holder of a CHI model 900B SECM. The array was placed in a SECM cell made of Teflon with the FTO/photocatalyst working electrode array exposed at the bottom through an O-ring. A Pt-wire and an Ag/AgCl electrode were used as counter and reference electrodes, and an air-saturated 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution was used as the electrolyte. Light from a 150 W xenon lamp was passed through the optical fiber, which was positioned perpendicular to the working electrode surface and illuminated onto the working electrode. The photocurrent produced by a constant photon flux during the scan was recorded and displayed as a two-dimensional image.

**Physicochemical Characterization.** X-ray diffraction (XRD) measurements were done using a Bruker-Norius D8 advanced diffractometer. The Cu K radiation source was operated at 40 kV and 40 mA. All measurements were carried out in the ( $\theta/2\theta$ ) mode. Samples for XRD were prepared by the drop cast method on a glass slide using the same solutions (100  $\mu\text{L}$  total) used to fabricate the arrays. Elemental analysis was carried out using a LEO 1530 scanning electron microscope equipped with an energy-disperse spectroscopy (EDS) system.

### 3. Results and Discussion

**SECM Studies on the Cu–In–Se System.** Spot arrays of the Cu–In–Se system with different ratios of Cu and In were fabricated with the dispenser and screened by SECM. As shown in Figure 1a, the numbers inside the circles represent the number of drops dispensed for that spot, where the first and second numbers represent the number of drops of solutions of CuCl<sub>2</sub> and InCl<sub>3</sub>, respectively. The 1st to 11th spots in the pattern represent compositions from 100% Cu to 100% In with 10% increments. Figure 1b, 1c, and 1d shows the SECM images obtained under UV–vis irradiation from the arrays after addition of the dimethylselenourea/hydrazine solution and annealed at different temperatures from 250 to 450 °C. The photocurrent images of CIS-250 and CIS-350 are similar. The cathodic photocurrent, which came from oxygen reduction, began to appear from the Cu 50/In 50 spot (the number values represent the atom percent of the element based on the solution added) and reached the maximum at the Cu 30/In 70 spot. The last two spots gave an oxidation current under irradiation, suggesting that the material in these two spots is n-type. Especially for the In 100% spot, the material should be In<sub>2</sub>Se<sub>3</sub>, which has been investigated widely as a n-type material. When the annealing temperature was increased to 450 °C, the reduction current improved remarkably. At the same time, the oxidation current at the last two spots disappeared. The cathodic photocurrent



**Figure 1.** (a) Dispensed pattern of CIS arrays. SECM images of (b) CIS-250, (c) CIS-350, and (d) CIS-450 under UV–vis light at an applied potential of  $-0.1$  V vs Ag/AgCl in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution.

**TABLE 1: Composition of Cu 50/In 50 and Cu 40/In 40 Spots in CIS-250 and CIS-450 Arrays Measured by EDS**

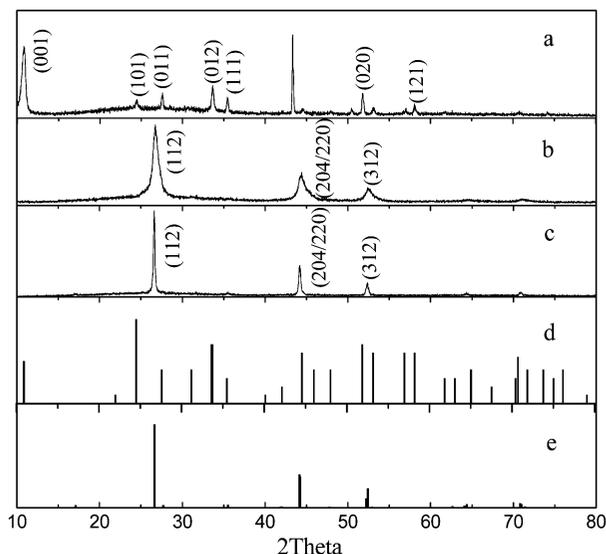
	sample	Cu:In:Se (mol ratio)
Cu 50/In 50	CIS-250	1:0.64:1.38
	CIS-450	1:0.22:0.44
Cu 40/In 60	CIS-250	1:1.34:1.83
	CIS-450	1:0.52:0.43

increased with addition of In with a maximum at the Cu 50/In 50 spot. As shown in Table 1, In and Se were heavily lost when the sample was annealed at 450 °C. This possibly led to the disappearance of oxidation current of the last spot. However, CIS-450 still had a higher photocurrent than that of CIS-250 and CIS-350. Perhaps high-temperature annealing produces bigger crystal grains that can depress electron–hole recombination.

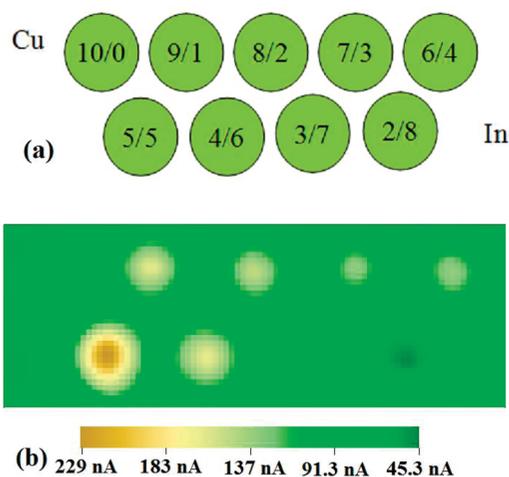
Figure 2 shows the XRD patterns of the samples prepared via pyrolysis of the mixture solution containing CuCl<sub>2</sub> and InCl<sub>3</sub> with and without dimethylselenourea. Most peaks in Figure 2a could be indexed to indium oxychloride. However, the spectra in Figure 2b and 2c match well with the standard XRD pattern of chalcopyrite CuInSe<sub>2</sub>, indicating conversion to the selenide form by the presence of dimethylselenourea:



The XRD results show that the materials of Cu 50/In 50 spots annealed at 250 and 450 °C possessed CuInSe<sub>2</sub> crystal structure.



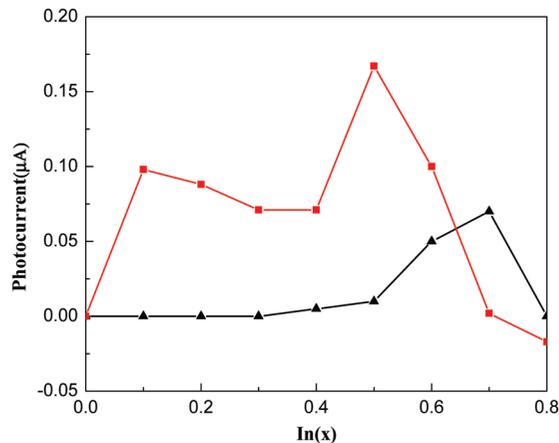
**Figure 2.** XRD patterns of the samples on glass slide substrates prepared by the drop cast method. The precursor solutions are CuCl<sub>2</sub>:InCl<sub>3</sub>, (ratio 1/1) (a) annealed at 250 °C without dimethylselenourea, (b and c) annealed at 250 and 450 °C with dimethylselenourea, respectively, (d) InOCl reference pattern (JCPDS No. 11-0510), (e) CuInSe<sub>2</sub> reference pattern (JCPDS No. 65-4869).



**Figure 3.** (a) Dispensed pattern of CdS-coated CIS array. (b) SECM image of CdS-coated CIS-250 array under UV-vis light at an applied potential of  $-0.1$  V vs Ag/AgCl in  $0.1$  M Na<sub>2</sub>SO<sub>4</sub> solution.

Compared with the sample annealed at 250 °C, the one annealed at 450 °C has narrower peaks, demonstrating better crystallinity, despite losing significant indium and selenium.

**CdS Deposition Studies on the Cu–In–Se System.** CdS is often deposited on the CuInSe<sub>2</sub> or CuIn<sub>x</sub>Ga<sub>1-x</sub>Se<sub>2</sub> film as a buffer layer to improve the energy efficiency in the preparation of thin film solid-state photovoltaic cells.<sup>16</sup> We tested this concept in PEC by depositing a CdS layer from a chemical bath on the top of the array to form a heterojunction with the array components. Figure 3a shows the dispensed pattern of the CdS-deposited CIS-250 array. Because the significant oxidation current of the Cu 10/In 90 and Cu 0/In 100 spots produced a very extended scale on the color bar so that it was difficult to discern differences in the reduction current of the array, the composition of CdS-coated CIS-250 array only varied from Cu 100/In 0 to Cu 20/In 80. Figure 3b shows the photocurrent of the CdS-deposited CIS-250 array and the absolute photocurrent value of the spots. Compared with CIS-250 without CdS deposition, the CdS layer clearly greatly improved the maximum

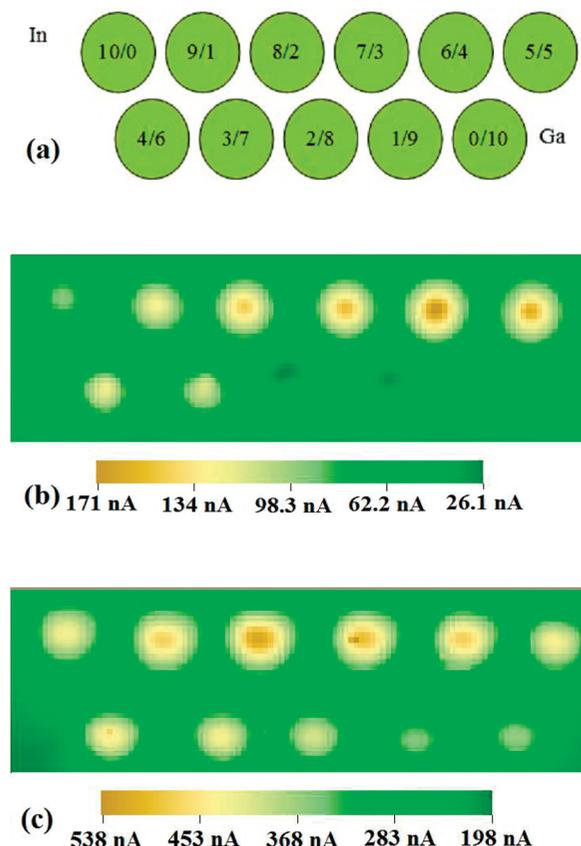


**Figure 4.** Profile of absolute photocurrents obtained from CIS-250 array (black line) and CdS-coated CIS-250 array (red line).

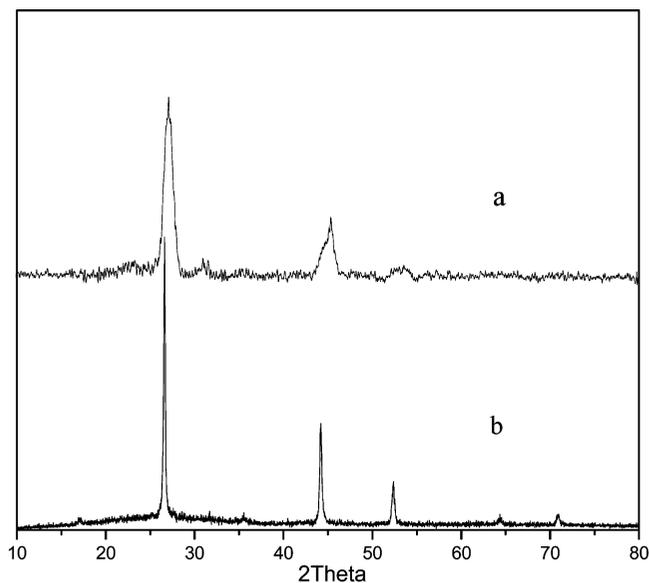
photocurrent. As shown in Figure 4, which compares results with and without CdS as a function of composition, the maximum photoreduction current moved to the Cu 50/In 50 spot and reached  $0.16$   $\mu$ A. The positive effect of the CdS layer has been attributed to surface modification of the spots, improving the separation of electrons and holes.<sup>18</sup>

**SECM Studies on the Cu–In–M–Se System (M = Ga, Zn, Cd).** Doping or alloying with additional elements is an effective method to improve a material's PEC properties.<sup>19</sup> However, the photocurrent is very sensitive to the nature and concentration of the doping element. An appropriate amount of Ga improves the energy conversion efficiency of a CuInSe<sub>2</sub> solar cell. In this study, we prepared a Cu–In–Ga–Se (CIGS) array and measured the photocurrent by SECM. Figure 5a shows the pattern of the Cu–In–Ga–Se array. Cu/In (1:1) and Cu/Ga (1:1) mixture solutions were prepared. The CIGS array with a varying ratio of In/Ga could be prepared by controlling the relative dispensing amount of two mixture solutions. The 1st to 11th spots in the pattern represent compositions from 100% CuInSe<sub>2</sub> to 100% CuGaSe<sub>2</sub> with 10% increments. Then the arrays were annealed at 250 and 450 °C. Figure 5b and 5c shows the SECM images of CIGS-250 and CIGS-450. According to the images, the In 60/Ga 40 spot and In 80/Ga 20 spot had the highest photocurrent in CIGS-250 and CIGS-450, respectively, which is close to previous reports, where  $x \approx 0.7$  produced the best results.<sup>20</sup> The photocurrent of CuInSe<sub>2</sub> was higher than that of CuGaSe<sub>2</sub> however. CuInSe<sub>2</sub> (1.04 eV) has a smaller band gap than CuGaSe<sub>2</sub> (1.7 eV), which will make CuInSe<sub>2</sub> absorb more photons and thus may be responsible for the higher photoactivity found with these spots. As shown in Figure 6, adding Ga made the diffraction peaks shift to the high-angle side, because the radius of Ga<sup>3+</sup> is smaller than that of In<sup>3+</sup>. It demonstrates that Ga entered into the lattice of CIS and formed a solid solution of CIGS. The growth of crystal was also restrained by the presence of Ga, so the CIGS sample showed broader peaks compared to CIS. The method of preparation of CIGS materials has a very strong effect on the efficiency and response, and the simple drop casting approach here is far from optimal (e.g., compared to vapor-phase methods).

Zn- and Cd-doped CIS-450 samples were also prepared and screened by SECM to test the doping elements effect on the photoelectrochemical property. Figure 7a shows the dispensed pattern of doped CIS arrays. First, 10 drops of Cu/In mixture solution were dispensed into every spot. Then different drops of  $0.01$  M Zn(NO<sub>3</sub>)<sub>2</sub> or Cd(NO<sub>3</sub>)<sub>2</sub> solution were added into the array so that the metal-doped CIS array had 1% increments from



**Figure 5.** (a) Dispensed pattern of photocatalyst spot array with different ratios of In and Ga. SECM image of (b) CIGS-250 and (c) CIGS-450 under UV-vis light at an applied potential of  $-0.1$  V vs Ag/AgCl in  $0.1$  M  $\text{Na}_2\text{SO}_4$  solution.

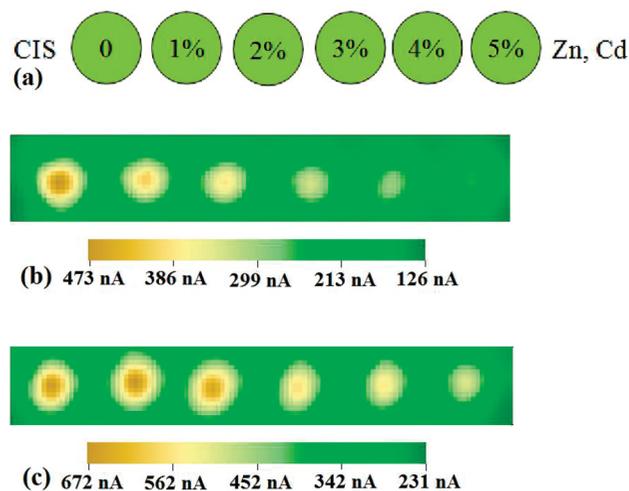


**Figure 6.** XRD pattern of the samples on glass slide substrates prepared by the drop cast method: (a)  $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$  and (b)  $\text{CuInSe}_2$ . Annealing temperature =  $450$  °C.

0 to 5%. As shown in Figure 7b and 7c, when Zn or Cd was added into CIS array the photocurrent decreased continuously as the doping concentration increased, indicating that Zn and Cd just produced a negative effect.

#### 4. Conclusions

We demonstrated a method for the rapid preparation of metal selenide spot arrays and investigation of their photoelectro-



**Figure 7.** (a) Dispensed pattern of photocatalyst spot array with different mol % Zn or Cd in CIS. SECM images of (b) Zn-doped and (c) Cd-doped CIS-450 arrays under UV-vis light at an applied potential of  $-0.1$  V vs Ag/AgCl in  $0.1$  M  $\text{Na}_2\text{SO}_4$  solution.

chemical properties. Rapid preparation was realized by making a spot array on FTO-coated glass using the robotic piezoelectric dispenser. Hydrazine provided an oxygen-free environment in the precursor solution and allowed preparation of the array under ambient air conditions without oxidation of dimethylselenourea used as the Se source. SECM results showed that different annealing temperatures affected the optimal spot position. When a thin layer of CdS was deposited on the CIS-250 array, the photoactivity of the spots was improved and the optimal spot moved from the Cu 70/In 30 to the Cu 50/In 50 spot. Furthermore, adding a certain amount of Ga (20%–40%) into the CIS array could increase the photocurrent, but Zn and Cd did not. This approach might be useful in improving the CIGS material by addition of still additional metals or anions or new surface treatments. The SECM array approach allows the rapid screening of such variations.

**Acknowledgment.** This material is based upon work supported by the Department of Energy under award number DE-SC0002219 and the Robert A. Welch Foundation (F-0021). G.L. thanks the National Scholarship Fund of the China Scholarship Council for support and advisor Prof. Liejin Guo from Xi'an Jiaotong University. Helpful discussions with Fu-Ren F. Fan are also gratefully acknowledged.

#### References and Notes

- (1) Repins, I.; Contreras, M. A.; Egaas, B.; DeHart, C.; Scharf, J.; Perkins, C. L.; To, B.; Noufi, R. *Prog. Photovoltaics* **2008**, *16*, 235.
- (2) Hollars, D. R.; Dorn, R.; Paulson, P. D.; Titus, J.; Zubeck, R. *Mater. Res. Soc. Symp. Proc.* **2005**, *865*, F14.34.1.
- (3) Liu, W.; Mitzi, D. B.; Yuan, M.; Kellock, A. J.; Chey, S. J.; Gunawan, O. *Chem. Mater.* **2010**, *22*, 1010.
- (4) Yokoyama, D.; Minegishi, T.; Maeda, K.; Katayama, M.; Kubota, J.; Yamada, A.; Konagai, M.; Domen, K. *Electrochem. Commun.* **2010**, *12*, 851.
- (5) Wang, J.; Yoo, Y.; Gao, C.; Takeuchi, I.; Sun, X.; Chang, H.; Xiang, X.-D.; Schultz, P. G. *Science* **1998**, *279*, 1712.
- (6) Danielson, E.; Golden, J. H.; McFarland, E. W.; Reaves, C. M.; Weinberg, W. H.; Wu, X. D. *Nature* **1997**, *289*, 944.
- (7) Woodhouse, M.; Herman, G. S.; Parkinson, B. A. *Chem. Mater.* **2005**, *17*, 4318.
- (8) Woodhouse, M.; Parkinson, B. A. *Chem. Mater.* **2008**, *20*, 2495.
- (9) Kleiman-Shwarsctein, A.; Hu, Y.; Forman, A. J.; Stucky, G. D.; McFarland, E. W. *J. Phys. Chem. C* **2008**, *112*, 15900.

- (10) Jang, J. S.; Yoon, K. Y.; Xiao, X.; Fan, F. R.; Bard, A. J. *Chem. Mater.* **2009**, *21*, 4803.
- (11) Jang, J. S.; Lee, J.; Ye, H.; Fan, F. R.; Bard, A. J. *J. Phys. Chem. C* **2009**, *113*, 6719.
- (12) Liu, W.; Ye, H.; Bard, A. J. *J. Phys. Chem. C* **2010**, *144*, 1201.
- (13) Pathirana, H. M. K. K.; Zingaro, R. A.; Meyers, E. A. *J. Electrochem. Soc.* **1993**, *140*, 2987.
- (14) Deng, Z.; Lie, F. L.; Shen, S.; Ghosh, I.; Mansuriper, M.; Muscat, A. J. *Langmuir* **2009**, *25*, 434.
- (15) Liu, G.; Liu, C.; Bard, A. J. Submitted to *J. Phys. Chem. C* for publication.
- (16) Ramanathan, K.; Contreras, M. A.; Perkins, C. L.; Asher, S.; Hasoon, F. S.; Keane, J.; Young, D.; Romero, M.; Metzger, W.; Noufi, R.; Ward, J.; Duda, A. *Prog. Photovoltaics: Res. Appl.* **2003**, *11*, 225.
- (17) Lee, J.; Ye, H.; Pan, S.; Bard, A. J. *Anal. Chem.* **2008**, *80*, 7445.
- (18) Kylner, A. *J. Appl. Phys.* **1999**, *85*, 6858.
- (19) Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* **2001**, *293*, 269.
- (20) Contreras, M. A.; Ramanathan, K.; AbuShama, J.; Hasoon, F.; Young, D. L.; Egaas, B.; Noufi, R. *Prog. Photovoltaics: Res. Appl.* **2005**, *13*, 209.

JP1058879