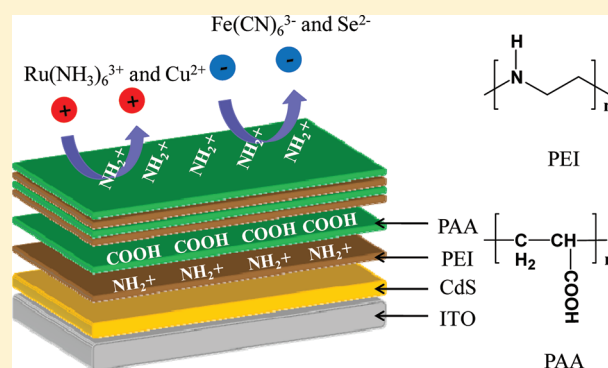


Sequential Chemical Bath Deposition of  $\text{Cu}_{2-x}\text{Se}/\text{CdS}$  Film by Suppressing Ion-Exchange ReactionGangri Cai,<sup>†</sup> Iseul Lim,<sup>†</sup> Deok Yeon Lee,<sup>†</sup> Nabeen K. Shrestha,<sup>†,‡</sup> Joong Kee Lee,<sup>‡</sup> Yoon-Chae Nah,<sup>§</sup> Wonjoo Lee,<sup>\*,†,‡</sup> and Sung-Hwan Han<sup>\*,†</sup><sup>†</sup>Department of Chemistry, Hanyang University, Seoul 133-791, Republic of Korea<sup>‡</sup>Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea<sup>§</sup>School of Energy•Materials•Chemical Engineering, Korea University of Technology and Education, Chungnam 330-708, Republic of Korea

**ABSTRACT:** Chemical bath deposition is an attractive technique to form single- and multilayered metal oxide/chalcogenide films on electrode surfaces. However, the occurrence of desorption and/or ion-exchange reaction during subsequent chemical bath deposition has so far limited preparation of multilayered metal oxide/chalcogenide films. In this paper, we report a method to prevent desorption and ion-exchange reaction of metal oxide/chalcogenide on electrode surfaces using a polyelectrolyte multilayer during sequential chemical bath deposition. By controlling the ion permeability of the polyelectrolyte multilayer,  $\text{Cu}_{2-x}\text{Se}$  film was successfully deposited on the CdS film. The  $\text{Cu}_{2-x}\text{Se}/\text{CdS}$  film is confirmed by UV–vis absorption spectroscopy, scanning electron microscopy, energy dispersive X-ray analysis, and X-ray powder diffractometer. Furthermore, the  $\text{Cu}_{2-x}\text{Se}/\text{CdS}$  films were investigated as photoinduced charge transfer devices which showed photocurrents of  $0.22 \text{ mA/cm}^2$  under illumination ( $I = 100 \text{ mW/cm}^2$ ).



## INTRODUCTION

Synthesis and formation of metal oxide/chalcogenide films on electrode surfaces is an important subject in the field of fundamental research with a wide range of applications.<sup>1,2</sup> Metal oxide/chalcogenide films have been utilized in light-emitting devices,<sup>3</sup> solar cells,<sup>4</sup> biological detection,<sup>5</sup> and other nanoscale devices.<sup>6</sup> To obtain high quality metal oxide/chalcogenide films on electrode surfaces, researchers have utilized numerous methods.<sup>1,2,6–9</sup> These methods can be primarily categorized in two processes. One is a vacuum-based process (denoted as vacuum process) and another one is a solution-based process (denoted as solution process). Compared to the vacuum processes, the solution process intrinsically has low production costs due to the required low temperatures and atmospheric processing conditions.<sup>1,2</sup> The representative solution processes are chemical bath depositions,<sup>1,2,7</sup> sol–gel,<sup>8</sup> spray pyrolysis,<sup>9</sup> electrodeposition,<sup>6</sup> etc.

Among these methods, chemical bath deposition is a soft solution process.<sup>1,2,4</sup> The fundamental growth mechanism of chemical bath deposition is similar to that of chemical vapor deposition, involving mass transport of reactants, adsorption, surface diffusion, reaction, nucleation, and growth. The chemical bath deposition is capable of producing high-quality thin film at a relatively low temperature. In addition, the chemical bath deposition has advantages such as being a simple and low-cost method to produce uniform, adherent, and reproducible large-area thin films for thin film electronics

applications. However, the fabrication of  $\text{Cu}_{2-x}\text{Se}/\text{CdS}$  multilayer films is not easy using chemical bath deposition. During the subsequent chemical bath depositions, the cation and/or anion in subsequent bath solutions attack the predeposited film due to further chemical activity.<sup>10–14</sup> In other words, desorption and/or ion-exchange reactions of the predeposited film can take place easily during subsequent chemical bath deposition. Consequently, the physical, chemical, and electronic properties of the metal chalcogenide films would be significantly changed by unwanted chemical reactions which generally lead to an unexpected performance of the devices. Therefore, it is highly desirable to develop a useful and effective method to control desorption and ion-exchange reactions during subsequent chemical bath deposition.

In the present study, a polyelectrolyte multilayer was investigated as an effective means to prevent desorption and ion-exchange reaction of the metal chalcogenide films during subsequent chemical bath deposition. The polyelectrolytes are polymers whose repeating units bear an electrolyte group.<sup>14–16</sup> These groups will dissociate in water, charging the polymers. Polyelectrolyte properties are thus similar to both electrolytes and polymers and are sometimes called polysalts. The chemical and physical properties of the polyelectrolyte multilayer can be

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controlled by various factors such as the structure of the polymer, the repetitive cycle, molecular weight and concentration of the polymer, treatment with a solution of a certain pH,<sup>14–16</sup> etc. For example, we recently reported the preparation of polyelectrolyte multilayers using polyethylene amine (PEI) and poly(acrylic acid) (PAA) and investigated the ion permeability of the PAA/PEI multilayer using swelling/shrinking of the polymer film by immersing in solutions of different pH.<sup>15,16</sup> Under basic conditions (pH = ~9), the carboxylic groups of PAA in the PAA/PEI multilayer are ionized completely, while amine groups in PEI are ionized only partially. In addition, it has been demonstrated that PEI layers can be swollen through columbic interactions, and PAA films can be changed into a compact structure by immersing the film into an acidic solution (pH = ~3). This phenomenon of swelling/shrinking of polymer films can selectively permeate ions in solution to PAA/PEI multilayers. Therefore, formation of a PAA/PEI multilayer on predeposited metal chalcogenide films can be an effective means to prevent unexpected chemical reactions during formation of Cu<sub>2-x</sub>Se film on CdS film by subsequent chemical bath deposition. On the basis of the previous observations and hypotheses, PAA/PEI multilayers were deposited on CdS film in the present work to prevent unwanted chemical reactions during formation of Cu<sub>2-x</sub>Se film by subsequent chemical bath deposition. Furthermore, CdS/Cu<sub>2-x</sub>Se film was investigated as a photoinduced charge transfer device.

## EXPERIMENTAL SECTION

**Chemical Bath Deposition of CdS Thin Film.** Chemicals were purchased from Aldrich and used as received. Indium–tin oxide (ITO, 10 Ω/square) electrodes were purchased from Samsung Corning Co. Chemical bath deposition of CdS<sup>4</sup> and Cu<sub>2-x</sub>Se<sup>17</sup> was carried out using the reported procedure. A 0.01 M CdCl<sub>2</sub> solution and 0.01 M thiourea solution were prepared in triple-distilled water. The pH of the solution was adjusted to ~9 by adding NH<sub>4</sub>OH solution. For the deposition of CdS films, cleaned ITO substrates were dipped into a beaker containing bath solution at 40 °C. After 120 min, the substrates were taken out of the bath, washed with deionized water, and dried in argon.

**Formation of Polyelectrolyte Multilayers on CdS Thin Film.** The polyelectrolyte multilayer was formed on CdS/ITO by repetitive cycles of the immersion of ITO substrates into polymer-containing solution as follows.<sup>15,16</sup> PEI (*M<sub>w</sub>*: 750 000) and PAA (*M<sub>w</sub>*: 3000) were used as positive and negative charge polymers. The CdS/ITO substrate was first immersed into PEI (0.1 M monomer concentration in deionized water) for 15 min and followed by rinsing with deionized water. Then it was immersed into the oppositely charged PAA (0.1 M monomer concentration in deionized water) solution for 15 min, followed by the same rinsing procedure. This dipping cycle was repeated *n* times to prepare (PAA/PEI)<sub>*n*</sub> on the CdS/ITO substrate. After the dipping cycle, the substrates were washed with deionized water and air-dried at room temperature.

**Chemical Bath Deposition of Cu<sub>2-x</sub>Se Thin Film on (PAA/PEI)<sub>*n*</sub>/CdS/ITO.** The chemical bath deposition of Cu<sub>2-x</sub>Se thin film on (PAA/PEI)<sub>*n*</sub>/CdS/ITO was carried out using the reported procedure.<sup>17</sup> A 0.1 M CuSO<sub>4</sub> solution and 0.1 M Na<sub>2</sub>SeSO<sub>3</sub> solution were separately prepared in triple-distilled water. The pH of the 0.1 M CuSO<sub>4</sub> solution was adjusted to ~3 by adding 1 M tartaric acid solution dropwise until the final pH was achieved. For preparation of 0.1 M

Na<sub>2</sub>SeSO<sub>3</sub> solution, sodium selenosulfate was formed by refluxing elemental selenium and sodium sulfite in water at 70 °C for 12 h with pH > 9. Then the two precursor solutions were mixed at equal volumes. The pH of the mixed solution was ~7. The (PAA/PEI)<sub>*n*</sub>/CdS/ITO substrates were immersed into a beaker containing bath solution at room temperature. After 120 min, the substrates were taken out of the bath, washed with deionized water, and dried in argon. Finally, the Cu<sub>2-x</sub>Se/(PAA/PEI)<sub>*n*</sub>/CdS film on ITO was sintered at 300 °C for 120 min under a N<sub>2</sub> environment to eliminate the polymer layers.

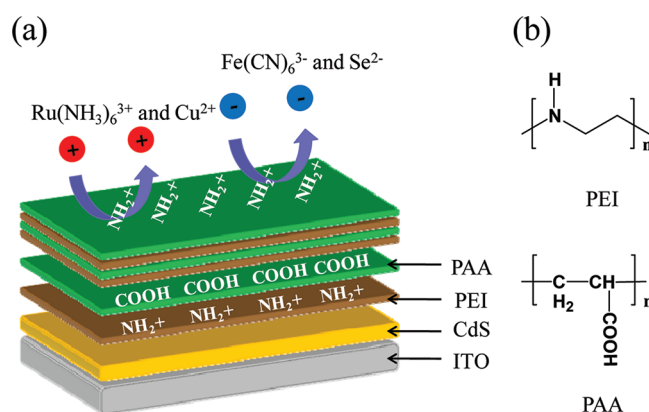
**Characterization.** The chemically deposited metal chalcogenide films were characterized using an X-ray powder diffractometer (XRD, Siemens D-5005 diffractometer), scanning electron microscopy (SEM, JEOL), a UV–vis absorption spectrometer (Varian, CARY 100), and an emission spectrometer (ISS Inc.).

The formation of polyelectrolyte multilayers on predeposited CdS thin film was monitored by cyclic voltammetry (Epsilon-EC). Electrochemical measurements were performed using a single-compartment three-electrode-system glass cell. A Ag/AgCl and Pt wire was used as reference electrode and counter electrode, respectively.

For performance measurement of photoinduced charge transfer devices, the Au metals were evaporated onto Cu<sub>2-x</sub>Se/CdS/ITO under ~10<sup>-6</sup> Torr. Photocurrent transients were obtained at a light intensity of 100 mW/cm<sup>2</sup> values with a white light with air mass (AM) 1.5 filters as a solar simulator in the presence of a water filter (450 W xenon lamp, Oriel Instruments), and the photocurrent was measured with a Keithley 2400 source meter.

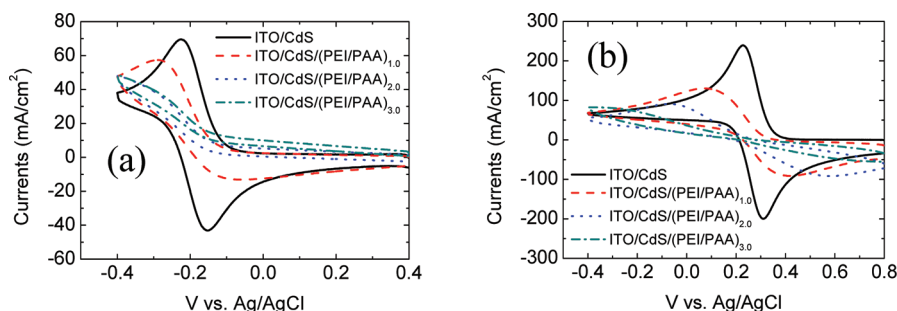
## RESULTS AND DISCUSSION

**Ion Permeability of Polyelectrolyte Multilayers on CdS/ITO.** Figure 1 shows the scheme of ion permeability in



**Figure 1.** (a) Schematic presentation of suppression of desorption and ion-exchange reaction of CdS film by PAA/PEI multilayers. (b) Chemical structure of PEI and PAA.

polyelectrolyte multilayers on CdS/ITO. The penetrations of ions in solution to polymer films were strongly influenced by surface charge and structure of polyelectrolyte multilayers.<sup>15,16</sup> The positively charged PEI layers prevent positively charged Cu<sup>2+</sup> ions in solution and attract the negatively charged Se<sup>2-</sup> ions in solution. On the other hand, the PAA layers in the polyelectrolyte multilayer are fully shrunk by treatment with the pH-adjusted acidic solution. The shrunk PAA has a compact



**Figure 2.** Cyclic voltammograms of (PAA/PEI)<sub>n</sub>/CdS/ITO in the presence of 1 mM (a) Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> or (b) Fe(CN)<sub>6</sub><sup>3-</sup> in 0.1 M KNO<sub>3</sub> solution at a scan rate of 50 mV/s.

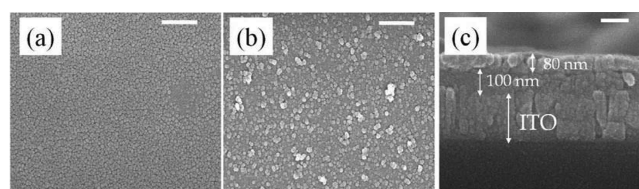
structure. Therefore, the Cu<sup>2+</sup> and Se<sup>2-</sup> ions in solution could not physically pass the compact PAA layer. Consequently, both the Cu<sup>2+</sup> and the Se<sup>2-</sup> ions in solution could not easily reach to the CdS surface through the polyelectrolyte multilayers. For these reasons, the surface charge and structure of polyelectrolyte multilayers are the critical factors to control the ion permeability during the chemical bath deposition of Cu<sub>2-x</sub>Se on CdS film.

To control the ion permeability of polyelectrolyte multilayers, the first layer in the PAA/PEI multilayer on CdS film was deposited as a PEI surface. Then, the PAA/PEI multilayer was treated with acidic solution (pH ~ 3). The ion permeability of the (PAA/PEI)<sub>n</sub> films was investigated using measurements of electrochemical behavior of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and Fe(CN)<sub>6</sub><sup>3-</sup> in acidic solution (pH = ~3). Figure 2a shows the cyclic voltammogram of (PAA/PEI)<sub>n</sub>/CdS/ITO in the presence of 1 mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>/0.1 M KNO<sub>3</sub> solution. The cyclic voltammogram of the CdS/ITO electrode without the polymer layers showed reversible redox reaction of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+/2+</sup>, and the potentials at maximum anodic ( $E_{pa}$ ) and cathodic currents ( $E_{pc}$ ) are -0.22 and -0.15 V, respectively, which is attributed to the redox reaction of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+/2+</sup>.<sup>15,16</sup> The half potential between  $E_{pa}$  and  $E_{pc}$  ( $E_{1/2}$ ) is 0.185 V. The maximum anodic ( $I_{pa}$ ) and cathodic current densities ( $I_{pc}$ ) at  $E_{pa}$  and  $E_{pc}$  in cyclic voltammogram of CdS/ITO electrode are 66.20 and 40.12 mA/cm<sup>2</sup>, respectively. In contrast, no clear characteristic redox peaks of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+/2+</sup> in the presence of the PAA/PEI multilayer on the CdS/ITO electrode can be seen in Figure 2a. Furthermore, the more the polymer layer was increased on the CdS/ITO surface, the more the current density was reduced in the cyclic voltammogram. This result indicates that Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> cannot penetrate to the polymer film due to swelling of PEI and shrinking of PAA in the PAA/PEI multilayer.

On the other hand, the measurement of cyclic voltammogram of (PAA/PEI)<sub>n</sub>/ITO were also carried out using 1 mM Fe(CN)<sub>6</sub><sup>3-</sup> in 0.1 M KNO<sub>3</sub> solution (Figure 2b). Two characteristic peaks appeared in the range 0.1–0.4 V, which is ascribed to a redox reaction of Fe(CN)<sub>6</sub><sup>3-/4-</sup>.<sup>15,16</sup> The  $E_{pa}$ ,  $E_{pc}$ ,  $E_{1/2}$ ,  $I_{pc}$ , and  $I_{pa}$  of the cyclic voltammogram of the CdS/ITO electrode without the polymer layer is 0.31 V, 0.22 V, 0.265 V, 284 mA/cm<sup>2</sup>, and 140 mA/cm<sup>2</sup>. Note that the tendency for current decrease in a cyclic voltammogram is similar to the case of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>. By the acidic treatment of the PAA/PEI multilayer, the PAA layers would be changed from a negative charge to a neutral state. In addition, the compact and dense structure of the PAA layer would be produced in the polyelectrolyte multilayer, leading to the minimization of the physical transport of ions through size discrimination. Fe(CN)<sub>6</sub><sup>3-</sup> is larger than 7 Å. Therefore, Fe(CN)<sub>6</sub><sup>3-</sup> may not

arrive easily to the CdS/ITO surface through neutral PAA layers. Consequently, the formation of polyelectrolyte multilayers on the CdS/ITO surface effectively controlled the penetration of the cations and anions in solution which successfully overcame the challenges of the formation of Cu<sub>2-x</sub>Se by subsequent chemical bath deposition.

**Morphological Properties.** The colors of CdS and Cu<sub>2-x</sub>Se films are dark yellow and bright brown, respectively. Figure 3 shows SEM images of CdS/ITO and Cu<sub>2-x</sub>Se/CdS/ITO.

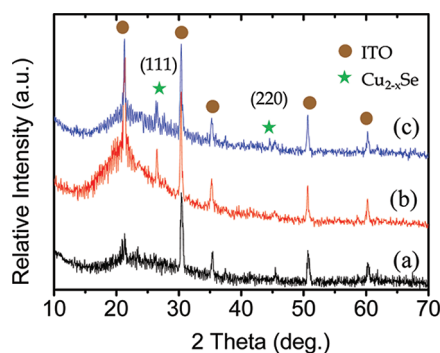


**Figure 3.** SEM images of (a) CdS/ITO (scale bar = 1000 nm) and (b) Cu<sub>2-x</sub>Se/CdS/ITO (scale bar = 1000 nm). (c) Cross-sectional SEM images of sample (b) (scale bar = 100 nm).

ITO. In Figure 3a, the uniform CdS were deposited on ITO film and have the size particles of ~80–100 nm. After deposition of Cu<sub>2-x</sub>Se film on the CdS/ITO surface, various sizes of particles were formed on the CdS/ITO surface. The size of Cu<sub>2-x</sub>Se particles on CdS/ITO is mainly ~50–100 nm (Figure 3b). In addition, the lump particles based on assembly of small particles appeared in the surface morphology of Cu<sub>2-x</sub>Se/CdS film, which have a size of ~500 nm. The thickness of CdS and Cu<sub>2-x</sub>Se is ~100 and 80 nm, respectively (Figure 3c). The thickness of polyelectrolyte multilayers in as-prepared Cu<sub>2-x</sub>Se/CdS would be ~8 nm.<sup>15,16</sup> However, the polymer film cannot be observed in the cross-sectional SEM image. This is because the polymer film between CdS and Cu–Se might have burned away during calcinations. Hence, the removal of the polymer film might be beneficial for charge transfer compared to an interface between Cu<sub>2-x</sub>Se and CdS films and polyelectrolyte multilayers.

**Structural Properties.** To confirm the structural properties, measurement of XRD of the CdS, Cu<sub>2-x</sub>Se, and Cu<sub>2-x</sub>Se/CdS/ITO films was carried out (Figure 4a,b). In all XRD patterns, a broad hump appears in the range of 15–35°, which may be attributed to amorphous glass and/or bilayer formation. The diffraction peaks do not appear in the XRD pattern of CdS film. In general, chemically deposited metal oxide/chalcogenide films are nanocrystalline.<sup>1,2</sup> On other hand, the XRD pattern of Cu<sub>2-x</sub>Se film shows diffraction peaks of (111) and (220) planes. The location of the peaks is in good agreement with the reference Cu<sub>2-x</sub>Se shown by the Joint Committee on Powder

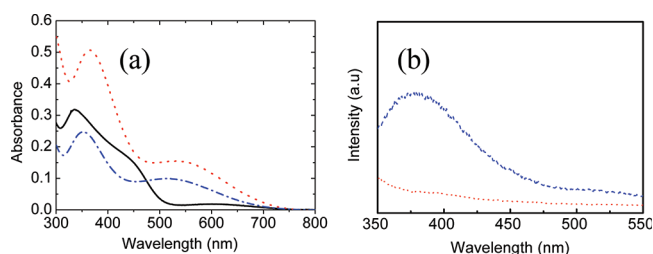




**Figure 4.** XRD pattern of (a) CdS/ITO, (b) Cu<sub>2-x</sub>Se/ITO, and (c) Cu<sub>2-x</sub>Se/CdS/ITO.

Diffraction Standard (JCPDS) [no. 06-0680] and confirms its berzelianite structure. The diffraction peaks of Cu<sub>2-x</sub>Se also appear in the XRD pattern of Cu<sub>2-x</sub>Se/CdS film. An average grain size of about 30 nm of Cu<sub>2-x</sub>Se on CdS film was obtained by averaging Scherrer's formula for all the observed (111) peaks.

**Absorption and Emission Properties.** UV-vis absorption spectra of CdS/ITO, Cu<sub>2-x</sub>Se/CdS/ITO, and Cu<sub>2-x</sub>Se/ITO electrodes are shown in Figure 5a. The wavelength with



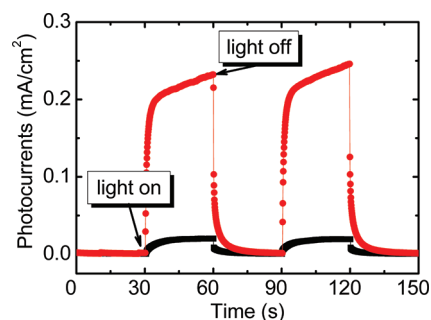
**Figure 5.** (a) UV-vis absorption and (b) emission spectra of CdS/ITO (solid), Cu<sub>2-x</sub>Se/ITO (dash), and Cu<sub>2-x</sub>Se/CdS/ITO (dot).

maximum absorbance from each film appears at ~351, 362, and 353 nm. The UV-vis absorption spectrum of CdS film on ITO is a little different from that of bulk CdS film, which may be attributed to a mixture of nano and bulk sizes. Note that the increase of absorption in Cu<sub>2-x</sub>Se/CdS/ITO appeared in the spectrum. It means that Cu<sub>2-x</sub>Se film is successfully deposited on CdS film in the presence of the PAA/PEI multilayer. However, the characteristic peak of CdS film does not appear in the UV-vis absorption spectrum of Cu<sub>2-x</sub>Se/CdS/ITO. This may be attributed to the overlap of absorption and/or bilayer formation of films.

To confirm photoinduced charge transfer effects of Cu<sub>2-x</sub>Se/CdS/ITO, the emission spectroscopy was measured using Cu<sub>2-x</sub>Se and Cu<sub>2-x</sub>Se/CdS film. Figure 5b shows the emission spectra of Cu<sub>2-x</sub>Se and Cu<sub>2-x</sub>Se/CdS film. The maximum peak in the emission spectrum of Cu<sub>2-x</sub>Se films is ~380 nm. On the other hand, the emission peak of Cu<sub>2-x</sub>Se films disappeared in the presence of CdS film. This result indicates effective charge transfer effects between Cu<sub>2-x</sub>Se and CdS films under illumination. The optical band gap of Cu<sub>2-x</sub>Se is ~2.7 eV.<sup>17</sup>

**Photoinduced Charge Transfer Devices.** On the basis of quenching results from the emission spectra, Cu<sub>2-x</sub>Se/CdS film can be applied as a photoinduced charge transfer device. For this, a Au film was deposited on Cu<sub>2-x</sub>Se/CdS film as counter electrode to fabricate the photoinduced charge transfer device.

As a reference, the Au/CdS/ITO devices were also prepared. To demonstrate photoinduced charge transfer in devices, *I*-*V* characterization can provide other useful information. In our experiments, however, the photovoltage of samples was too small to gather meaningful information. Therefore, we tried an alternative method (i.e., photocurrent transient) to verify the photoinduced effects of samples. Both of these devices effectively responded under illumination and darkness (Figure 6). Cu<sub>2-x</sub>Se/CdS film produces photocurrents of 0.22 mA/cm<sup>2</sup>.



**Figure 6.** Photocurrent density of Au/CdS/ITO (■) and Au/Cu<sub>2-x</sub>Se/CdS/ITO (●) as a function of time (*I* = 100 mW/cm<sup>2</sup>).

In contrast, CdS film without the Cu<sub>2-x</sub>Se layer generates photocurrents of 0.02 mA/cm<sup>2</sup>. The significantly higher photocurrents of Cu<sub>2-x</sub>Se/CdS film can be attributed to the effective charge transfer effects by formation of Cu<sub>2-x</sub>Se film on CdS film. Furthermore, the photocurrent improvement could be also due to the smaller band gap of Cu<sub>2-x</sub>Se.

## CONCLUSIONS

In summary, we reported a novel approach to fabricate layered Cu<sub>2-x</sub>Se/CdS films using a polyelectrolyte multilayer. Furthermore, the layered Cu<sub>2-x</sub>Se/CdS films were investigated for photoinduced charge transfer devices. The formation of a polyelectrolyte multilayer on CdS/ITO efficiently controlled the desorption and/or ion-exchange reaction during the subsequent chemical bath deposition. Consequently, the Cu<sub>2-x</sub>Se film was successfully deposited on the CdS/ITO surface in the presence of the polyelectrolyte multilayer. The resultant Cu<sub>2-x</sub>Se/CdS film showed photocurrents of 0.22 mA/cm<sup>2</sup> under illumination (*I* = 100 mW/cm<sup>2</sup>). Investigations of the Cu<sub>2-x</sub>Se/CdS film on the extremely thin absorber solar cells are currently underway. We believe that the present approach can be applied equally for controlling ion permeability in other solution systems to fabricate a variety of multilayered metal oxide/chalcogenide films.

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### Notes

The authors declare no competing financial interest.

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