

# Cu<sub>2</sub>O Nanowires in an Alumina Template: Electrochemical Conditions for the Synthesis and Photoluminescence Characteristics

Eunseong Ko,<sup>[b]</sup> Jinsub Choi,<sup>[c]</sup> Koichi Okamoto,<sup>[d]</sup> Yongsug Tak,<sup>[b]</sup> and Jaeyoung Lee<sup>\*[a]</sup>

*Cu<sub>2</sub>O nanowires, mainly consisting of (100) and (200) polycrystalline structures with a length of 4 μm are prepared by electrochemical deposition using a porous alumina template. It is found that the optimized electrochemical conditions to prepare Cu<sub>2</sub>O nanowires are different from those for the formation of a bulk thin Cu<sub>2</sub>O layer since different pH values are found between the tip of the pores and the bulk, due to diffusion limits in porous*

*alumina with an extremely high aspect ratio of 300. We point out that Cu<sub>2</sub>O (200), Cu<sub>2</sub>O (111), Cu, and co-deposited alloys can be obtained under specific electrochemical conditions. In addition, the optical band gap of the prepared Cu<sub>2</sub>O nanowires with a length of 4 μm and a diameter of 200 nm is estimated to be 2.17 eV from photoluminescence measurements.*

## 1. Introduction

Nanowires with a high aspect ratio within a range between one and a few hundreds of nanometers have attracted growing interest owing to their distinct, attractive properties, as well as their unique applications compared with bulk materials.<sup>[1,2]</sup> It is expected that nanowires will play an important role as both interconnectors and active components in fabricating nanoscale devices. Furthermore, the formation of nanoporous alumina templates by electrochemical oxidation of aluminum has been of great interest for the fabrication of highly ordered nanosized materials in biological, electronic, thermoelectric, and photonic devices.<sup>[3–5]</sup> This increased attraction in porous alumina as a template is mainly due to the simple and low-cost manufacturing process. Nanowires of metals,<sup>[6–9]</sup> semiconductors,<sup>[10,11]</sup> and polymers<sup>[12]</sup> have been synthesized in hexagonally ordered nanoporous alumina templates by several research groups; in particular, the preparation of metal oxide nanowires such as Cu<sub>2</sub>O in alumina templates by electrodeposition was recently reported.<sup>[13,14]</sup>

Cu<sub>2</sub>O is a non-stoichiometric p-type semiconductor with a band gap of 2.0 eV which has been proposed as a photocatalytic material for splitting water into H<sub>2</sub> and O<sub>2</sub> via visible light irradiation.<sup>[15–17]</sup> It is also a potential material for fabrication of low-cost solar cells.<sup>[18,19]</sup>

Herein, we investigated the influence of pH solution and applied current density on the formation of Cu<sub>2</sub>O nanowires in an alumina template/Pt substrate.

## Experimental Section

Cu<sub>2</sub>O nanowires were electrochemically deposited onto porous alumina membranes using a conventional three-electrode system. A platinum metal layer with a thickness of a few hundreds of nano-

meters was deposited on one side of a commercial alumina membrane (Whatman, Anodisc 25) with a diameter of 200 nm by direct current (DC) sputtering (Nuricell Inc., Korea). The sputtered Pt layer, the saturated calomel electrode (SCE), and the platinum mesh were employed as the working electrode, the reference electrode, and the counter electrode, respectively. In order to prepare Cu<sub>2</sub>O, a total of 45 g of 99.99% CuSO<sub>4</sub> (Aldrich) was dissolved in 75 mL of 88% lactic acid (Aldrich) and thereby stabilizing the copper ions with lactate ions. Aqueous sodium hydroxide solution (5 M; Aldrich) was added to adjust the pH to 6.0–12.0.

A potentiostat-galvanostat (EG&G PAR 273A) was used to apply a current density of  $-0.1$  to  $-0.5$  mA cm<sup>-2</sup> for the deposition of Cu<sub>2</sub>O. The solution temperature of 65 °C was maintained during the experiments. The surface morphology of the prepared nanowires was analyzed by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4300). The crystallinity and quantitative analysis of the metal oxides were carried out using X-ray diffraction (XRD, Phillips DY616) and energy dispersive X-ray spectroscopy (EDX) coupled with the SEM equipment. Photoluminescence measurements were performed to estimate the optical band gap of Cu<sub>2</sub>O

[a] Dr. J. Lee  
Fuel Cell Research Center, Korea Institute of Science and Technology  
Seoul 136-791 (South Korea)  
Fax: (+82)2-958-5199  
E-mail: jaeyoung@kist.re.kr

[b] E. Ko, Prof. Y. Tak  
Department of Chemical Engineering, Inha University  
Inchon 402-751 (South Korea)

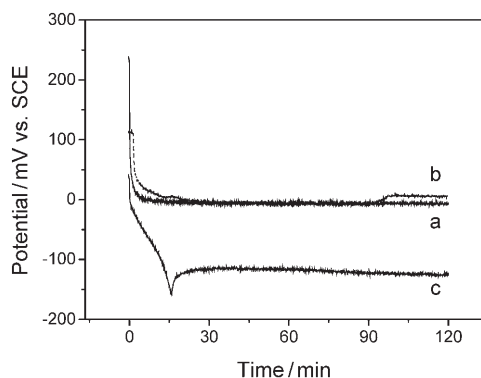
[c] Dr. J. Choi  
Nanomaterials Application Division  
Korea Institute of Ceramic Engineering and Technology  
Seoul 153-801 (South Korea)

[d] Dr. K. Okamoto  
Division of Engineering and Applied Science  
California Institute of Technology  
Pasadena CA 91125 (USA)

nanowires. An InGaN laser (wavelength: 405 nm, and power: 4.5 mW) was used as excitation source and a spectrometer (10 micron slit width, 300 Lmm<sup>-1</sup> grating) exit with a liquid nitrogen-cooled CCD camera (Spec 10:100B, Princeton Instruments) was employed as detector. For a distinct signal, optical filters were used to cut-off a wavelength shorter than  $\approx 440$  nm.

## 2. Results and Discussion

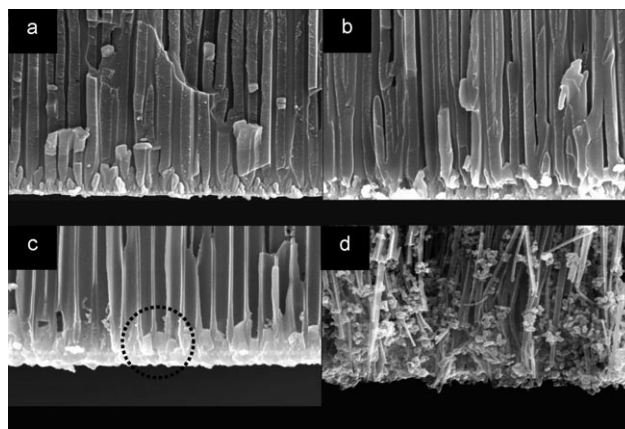
Figure 1 shows the potential transients during electrochemical deposition performed at  $-0.1 \text{ mA cm}^{-2}$  and at different pH solutions. In the case of solutions at pH 6.0 and 8.0, the transients



**Figure 1.** Potential transients during electrochemical deposition performed at  $-0.1 \text{ mA cm}^{-2}$  at a) pH 6, b) pH 8, and c) pH 10 in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  + lactic acid + NaOH for 4 h.

achieve the steady state potential value of 0.0 V after a sharp cathodic increase of several seconds. It was reported that such a dramatic increase of potential at the initial stage arises from the overpotential for the nucleation of nanowires.<sup>[20]</sup> In pH 8.0 solution, a decrease of the cathodic current is observed after 1.5 h, suggesting that the current flow could pass more easily through the nanowires/alumina composite probably due to the growth of  $\text{Cu}_2\text{O}$  nanowires on the top of the alumina or to the creation of a shortcut caused by breakdown of the oxide. For the solution at pH 10.0, the potential increases at the beginning of the electrochemical deposition and further increases by  $-150$  mV. After reaching a maximum, the potential significantly decays, indicating that the continuous growth of  $\text{Cu}_2\text{O}$  nanowires is interrupted for the reasons discussed above.

Morphological investigations were performed to support the interpretation of the potential transients. The cross-sectional view of the alumina template/Pt composite prepared at  $-0.1 \text{ mA cm}^{-2}$  and at different pH solutions is shown in Figure 2. We were not able to observe any materials deposited on the alumina template (see Figures 2a and 2b), whereas a very small amount of deposited materials was exhibited near the bottom of the alumina template/Pt substrate, as shown in Figure 2c (see the dotted circles). As we expected from the interpretation of the potential transient of Figure 1c, small particles well distributed inside the alumina template were observed in the top part of the sample prepared at pH 10 (see Figure 2d). These particles are revealed as a copper-oxygen

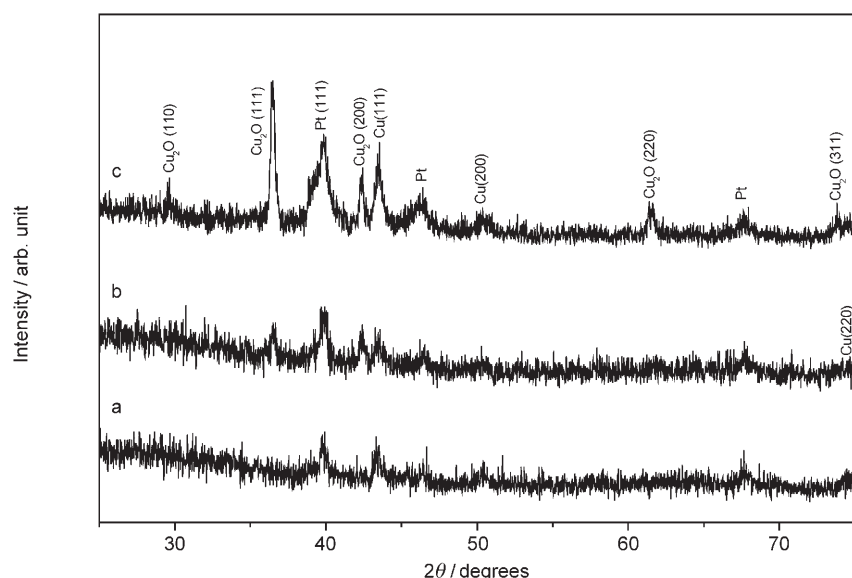


**Figure 2.** Cross-sectional SEM observations of the lower region of  $\text{Cu}_2\text{O}$ /alumina template composites. a), b), and c) show the results obtained under the deposition conditions of Figures 1a, 1b, and 1c, respectively; d) is the upper region of (c).

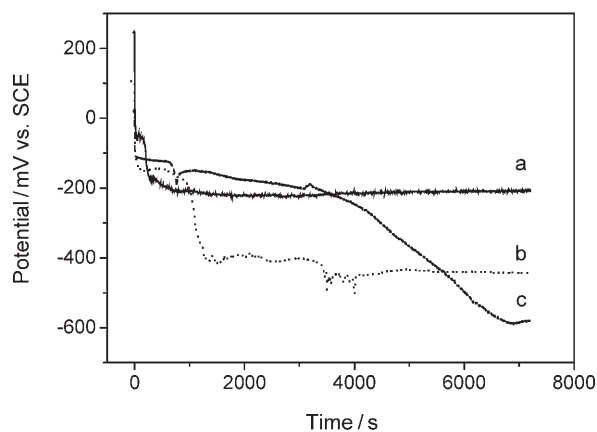
composite, that is,  $\text{Cu}_2\text{O}$  or  $\text{Cu}(\text{OH})$ , from EDX data (not shown here). The results demonstrate that the dramatic decrease of potential in Figure 1c is caused by the formation of  $\text{Cu}_2\text{O}$  nanowires on the surface of the alumina.

Figure 3 shows the XRD structural data of the samples prepared at  $-0.1 \text{ mA cm}^{-2}$ . A weak peak, assigned to Cu metal, is only detected in the sample prepared at pH 6.0. However,  $\text{Cu}_2\text{O}$  peaks appear in the sample prepared at pH 8.0 even though they are relatively weak compared to the Cu and Pt (substrate) peaks. In the case of the sample prepared at pH 10.0,  $\text{Cu}_2\text{O}$  peaks become dominant, indicating that  $\text{Cu}_2\text{O}$  (111) preferentially forms. From the SEM observation, the XRD analysis, and the Pourbaix diagram,<sup>[21]</sup> we can assume that Cu and  $\text{Cu}_2\text{O}$  are co-deposited on porous alumina at  $-0.1 \text{ mA cm}^{-2}$ . This is due to the lower concentration of hydroxide ions present in weak alkaline conditions (see the detailed discussion on the mechanism in the following section).

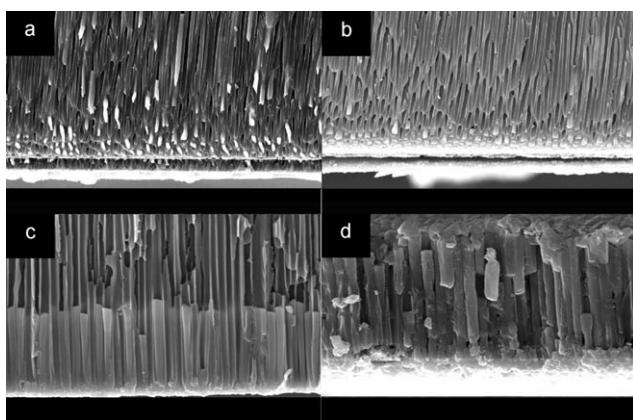
Therefore, in some experiments aimed at increasing the local interface pH, we applied a higher current density of  $-0.5 \text{ mA cm}^{-2}$ . Compared to the potential transients displayed in Figures 4a and b, Figure 4c shows that the potential continuously increases over 2 h and reaches a maximum value of  $-580$  mV. Since the increase of cathodic potential stems from the potential drop resulting from the continuous growth of nanowires, we suggest that  $\text{Cu}_2\text{O}$  nanowires continuously grow in solutions of pH 10.0. The formation of  $\text{Cu}_2\text{O}$  nanowires under these conditions is confirmed by the morphological observations of alumina templates (see Figure 5). Figures 5a and 5b show SEM observations near the Pt layer deposited on one side of the alumina template, revealing that the nanowires are randomly formed in solutions of pH 6.0 and 8.0. Using a pH 10.0 solution,  $\text{Cu}_2\text{O}$  nanowires in alumina template are observed (Figure 5c). Each nanowire has a similar length of approximately  $4 \mu\text{m}$  without disconnection; the average aspect ratio of the nanowires is estimated to be 20. When the cathodic charge is doubled, (i.e. a longer deposition time is used), in order to make  $\text{Cu}_2\text{O}$  nanowires with the higher aspect ratio, the alumina template is completely dissolved. Note that the



**Figure 3.** XRD data of materials deposited on alumina template. The electrochemical deposition was conducted at applied current density of  $-0.1 \text{ mA cm}^{-2}$  for 4 h at a) pH 6, b) pH 8, c) pH 10.



**Figure 4.** Potential transients during electrochemical deposition performed at  $-0.5 \text{ mA cm}^{-2}$  at a) pH 6, b) pH 8 and c) pH 10 for 2 h. The electrolyte is the same as that of Figure 1.

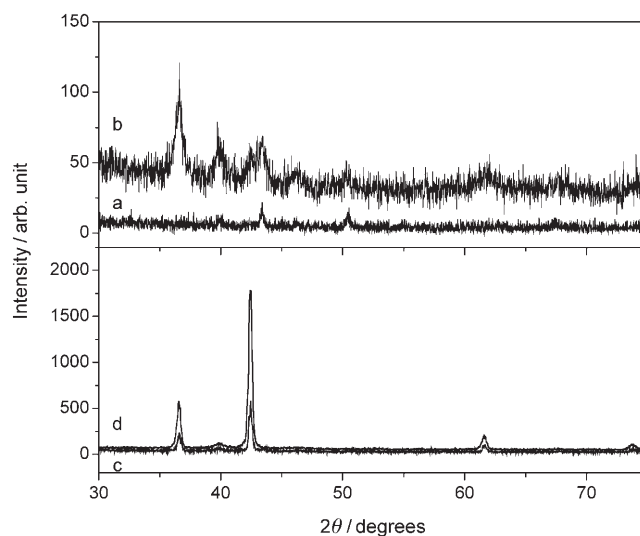


**Figure 5.** SEM cross-sectional view of Cu<sub>2</sub>O and/or Cu prepared at  $-0.5 \text{ mA cm}^{-2}$  at a) pH 6, b) pH 8, c) pH 10. In (c), Cu<sub>2</sub>O nanowires with a length of  $4 \mu\text{m}$  are visible.

anodic alumina structure can be completely destroyed by chemical dissolution when it is exposed to strongly alkaline solutions ( $\text{pH} \geq 8.0$ ) at high temperatures ( $T \geq 30^\circ\text{C}$ ).<sup>[22]</sup> This leads to the formation of free standing Cu<sub>2</sub>O nanowires on the Pt substrate as shown in Figure 5 d.

We believe that the initial growth rate of Cu<sub>2</sub>O nanowires is not significant since only seeds of Cu<sub>2</sub>O nanowires are observed after 1 h, whereas Cu<sub>2</sub>O nanowires with a length of  $4 \mu\text{m}$  are exhibited after 2 h as discussed above. This result is in good agreement with the observation that the slope of the potential increase in Figure 4 c is distinctly changed after 1 h.

The structural analysis of the samples prepared at  $-0.5 \text{ mA cm}^{-2}$  is shown in Figure 6. Here is observed the same tendency as in Figure 3, the more basic the electrolyte the



**Figure 6.** XRD data of Cu<sub>2</sub>O nanowires prepared at  $-0.5 \text{ mA cm}^{-2}$  for 2 h at a) pH 6, b) pH 8 and c) pH 10. d) XRD data of Cu<sub>2</sub>O nanowires at  $-0.5 \text{ mA cm}^{-2}$  for 4 h at pH 10.

more distinct are the Cu<sub>2</sub>O peaks. Perfect polycrystalline Cu<sub>2</sub>O nanowires are obtained at pH 10, independently of the deposition time (see Figures 6 c and 6 d). However, if the electrolyte is extremely alkaline, only Cu metal is detected.

#### Mechanism of Formation of Cu<sub>2</sub>O in Porous Alumina

The mechanism of formation of Cu<sub>2</sub>O on a bulk substrate by electrochemical deposition has been studied by several re-

search groups.<sup>[15,23–25]</sup> It has been reported that the electrochemical reaction to form Cu<sub>2</sub>O takes more than one step [see Eqs. (1)–(3)]:



A higher solution pH enhances the reduction of cupric ion (Cu<sup>2+</sup>) to cuprous ion (Cu<sup>+</sup>) as described in Reaction (1). If the pH is lower than the pH at which Reaction (1) takes place, Cu metal is deposited via two successive one-electron reduction reactions, due to the less than optimal production of hydroxide ions. However, we suppose that at pH ≈ 12.0, either Cu<sub>2</sub>O is further reduced to Cu metal (since Cu<sub>2</sub>O is unstable at extremely high pH) or Cu metal is deposited, since the soluble complex formed between Cu<sup>2+</sup> and the organic acid anion is not formed at high pH.

It is reasonable to assume that the pH is different at the tip of the pores than in the bulk due to diffusion limits in porous alumina with extremely high aspect ratio. Therefore, optimized electrochemical preparative conditions for Cu<sub>2</sub>O nanowires are different from those for the formation of a bulk thin layer. In fact, Switzer and co-workers have reported that Cu<sub>2</sub>O (100) and Cu<sub>2</sub>O (111) on bulk substrates are obtained at pH values of 9.0 and 12.0, respectively.<sup>[23]</sup> In our case, Cu<sub>2</sub>O (200), Cu<sub>2</sub>O (111), Cu, or co-deposited alloys are obtained employing the electrochemical conditions summarized in Table 1.

**Table 1.** Summary of the electrochemical conditions for the preparation of Cu<sub>2</sub>O nanowires.

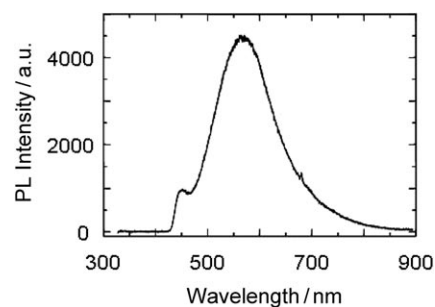
	Current density [mA cm <sup>-2</sup> ]	
	-0.1	-0.5
pH 6	Cu	Cu
pH 8	Cu, Cu <sub>2</sub> O(111)	Cu <sub>2</sub> O(111) > Cu <sub>2</sub> O(200)
pH 10	Cu, Cu <sub>2</sub> O(111) < Cu <sub>2</sub> O(200)	Cu <sub>2</sub> O(111) < Cu <sub>2</sub> O(200)
pH 12	Cu	Cu

### Photoluminescence Measurements of Cu<sub>2</sub>O in Porous Alumina

As mentioned in the introduction, Cu<sub>2</sub>O is reported as a non-stoichiometric p-type semiconductor with a direct band gap of 2.0 eV. Figure 7 shows photoluminescence spectra of Cu<sub>2</sub>O nanowires in porous alumina template, which was prepared at -0.5 mA cm<sup>-2</sup> and pH 10 for 2 h. We observe that the maximum occurs at 572 nm, corresponding to the optical band of 2.17 eV.

### 3. Conclusions

Electrochemical conditions for the synthesis of Cu<sub>2</sub>O in a porous alumina template have been elucidated and discussed



**Figure 7.** Photoluminescence measurements of Cu<sub>2</sub>O nanowires prepared at -0.5 mA cm<sup>-2</sup> for 2 h at pH 10.

in detail. We postulate that the different conditions for the preparation of Cu<sub>2</sub>O are caused by geometrical factors, for example, a local pH change at the tip of the pores caused by the diffusion limits in long channels of porous alumina.

In both cases, that is, -0.1 and -0.5 mA cm<sup>-2</sup>, Cu<sub>2</sub>O nanowires can only be prepared in a pH range from 8 to 10. Deviations from the preferred pH range lead to the deposition of Cu metal. In particular, perfect polycrystalline Cu<sub>2</sub>O nanowires, mainly consisting of (200) and (111) structures, are obtained when the electrochemical deposition is performed under the conditions: solution at pH 10, current density of -0.5 mA cm<sup>-2</sup>, and electrochemical deposition time of 2 h. Using the optimized conditions, polycrystalline Cu<sub>2</sub>O nanowires with a length of 4 μm are obtained. Applying electrolysis times longer than 2 h, free standing nanowires are formed due to the complete dissolution of the alumina membrane in the extreme conditions of high pH and high temperature. Photoluminescence spectra of Cu<sub>2</sub>O nanowires are measured, showing that the optical band gap of Cu<sub>2</sub>O nanowires is around 2.17 eV which is in good agreement with the literature.

### Acknowledgements

This work was supported by the Korea Science and Engineering Foundation under a grant from the Engineering Research Center for Energy Conversion and Storage.

**Keywords:** electrochemistry · mesoporous materials · metal oxides · nanowires · X-ray diffraction

- [1] S. J. Tans, R. M. Verschuere, C. Dekker, *Nature* **1998**, 393, 49.
- [2] H. Dai, E. W. Wong, Y. Z. Lu, S. Fan, C. M. Lieber, *Nature* **1995**, 375, 769.
- [3] J. Choi, Y. Luo, R. B. Wehrspohn, R. Hillebrand, J. Schilling, U. Gösele, *J. Appl. Phys.* **2003**, 94, 4757.
- [4] J. Malicka, I. Cryczynski, J. Kusba, Y. B. Shen, J. R. Lakowicz, *Biochem. Biophys. Res. Commun.* **2002**, 294, 886.
- [5] H. Masuda, M. Ohya, H. Asoh, M. Nakao, M. Nohtomi, T. Tamamura, *Jpn. J. Appl. Phys., Part 1* **1999**, 38, L1403.
- [6] J. Choi, G. Sauer, K. Nielsch, R. B. Wehrspohn, U. Gösele, *Chem. Mater.* **2003**, 15, 776.
- [7] K. Nielsch, F. Müller, A. P. Li, U. Gösele, *Adv. Mater.* **2000**, 12, 582.
- [8] Y. Zhang, G. Li, Y. Wu, B. Zhang, W. Song, L. Zhang, *Adv. Mater.* **2002**, 14, 1227.
- [9] M. S. Sander, A. L. Prieto, R. Gronsky, T. Sands, A. M. Stacy, *Adv. Mater.* **2002**, 14, 665.

- [10] B. R. Martin, D. J. Dermody, B. D. Reiss, M. Fang, L. A. Lyon, M. J. Natan, T. E. Mallouk, *Adv. Mater.* **1999**, *11*, 1021.
- [11] M. S. Sander, R. Gronsky, T. Sands, A. M. Stacy, *Chem. Mater.* **2003**, *15*, 335.
- [12] M. Steinhart, J. H. Wendorff, A. Greiner, R. B. Wehrspohn, K. Nielsch, J. Schilling, J. Choi, U. Gösele, *Science* **2002**, *296*, 1997.
- [13] J. Oh, Y. Tak, J. Lee, *Electrochem. Solid-State Lett.* **2004**, *7*, C27.
- [14] J. Oh, Y. Tak, J. Lee, *Electrochem. Solid-State Lett.* **2005**, *8*, C81.
- [15] P. E. de Jongh, D. Vanmaekelbergh, J. J. Kelly, *Chem. Mater.* **1999**, *11*, 3512.
- [16] P. E. de Jongh, D. Vanmaekelbergh, J. J. Kelly, *Chem. Commun.* **1999**, 1069.
- [17] M. Hara, T. Konto, M. Komoda, S. Ikeda, K. Shinohara, A. Tanaka, J. N. Kondo, K. Domen, *Chem. Commun.* **1998**, 2185.
- [18] A. O. Musa, T. Akomolafe, M. J. Carter, *Sol. Energy Mater. Solar Cells* **1998**, *51*, 305.
- [19] K. Santra, P. Chatterjee, S. P. Sen Gupta, *Sol. Energy Mater. Solar Cells* **1999**, *57*, 345.
- [20] G. Sauer, G. Brehm, S. Schneider, K. Nielsch, R. B. Wehrspohn, J. Choi, H. Hofmeister, U. Gösele, *J. Appl. Phys.* **2002**, *91*, 3243.
- [21] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, NACE, Houston, **1974**.
- [22] P. A. Malachuk in *Encyclopedia of electrochemistry of the elements*, Vol. VI (Ed.: A. J. Bard), Marcel Dekker, New York, **1973**.
- [23] T. D. Golden, M. G. Shumsky, Y. Zhou, R. A. VanderWerf, R. A. Van Leeuwen, J. A. Switzer, *Chem. Mater.* **1996**, *8*, 2499.
- [24] J. Lee, Y. Tak, *Electrochem. Solid-State Lett.* **2000**, *3*, 69.
- [25] J. Lee, J. Oh, Y. Tak, *J. Ind. Eng. Chem.* **2004**, *10*, 1058.

---

Received: January 31, 2006

Published online on May 30, 2006