Efficiency Optimization on Dye-Sensitized Solar Cells With Low-Frequency Noise Analysis

Szu Cheng Lai, Ming Fei Yang, Surani Bin Dolmanan, Lin Ke, and Xiao Wei Sun, *Senior Member, IEEE*

Abstract—The effects of time durations for ZnO nanorod growth and dye loading on a ZnO-based dye-sensitized solar cell's efficiency and $1/f$ low-frequency noise (LFN) spectral were analyzed. Sufficient time durations for ZnO growth and dye loading were required for achieving optimum photoconversion efficiency. Extending these two time parameters beyond the optimal, however, reduced the efficiency due to nanorod defects and dye agglomerations. The mechanisms inducing the change in the efficiency was reflected in the LFN spectral and explained on the basis of Kleinpenning's noise equation and excessive noises in the presence of structural defects.

Index Terms—Dye loading, dye-sensitized solar cells, ZnO nanorods, 1/f noise.

I. INTRODUCTION

A dye-sensitized solar cell (DSSC) [1] is developed by diffusing dye molecules into a mesoporous layer of ZnO or $TiO_2 f$ nanorods to form a photoactive surface for photocurrent generation. The nanorods must possess a high aspect ratio to enlarge the dye coverage area and enhance the anchorage of the dye. In fabricating a DSSC wherein the nanorods are grown by the precipitation method, it is important to control the durations for nanorod growth and dye loading because these determine the nanorod length and dye uptake, respectively.

The nanorod growth occurred in three phases [2]: 1) solution stabilizes and nucleation begins; 2) nanorods linearly grow with time; and 3) growth decline due to depletion of the precursors for crystalline growth or limitation imposed by the randomly orientated surrounding nanorods. Insufficient growth time results in nanorods with low aspect ratio and poor coverage on the underlying anode film. Extended growth time, however, induces dissolution effects on the nanorods, resulting in shorter length, structural defects, and weakening of interfacial bond between the nanorods and anode layers. Likewise, dye loading involved three procedures [3]: 1) diffusion of the dye into the nanorod layer; 2) adsorption of the dye onto the surface; and 3) agglomeration of the dye. A suitable loading time allows the dye to diffuse into the mesoporous structure and cover on the nanorod surface in the monolayer. Too long loading time, however, reduces the efficiency due to shielding effects from the extra dye, which blocks the underlying dye adsorbed on the nanorods from solar irradiance. For the ZnO DSSC, the acidic dye dissolves the metal oxide to form Zn^{2+}/dye complexes [3] in the pores of the nanorod layer. These complexes cause poor electron injection and thus reduce the device quality in terms of conversion efficiency.

The effects of nanorod growth time and dye-loading time on efficiency had been well studied, but little attempts were made to analyze the issue based on low-frequency noise (LFN). It is known that low-frequency $1/f$ noise is very sensitive to microscopic imperfections of a material and is a figure of merit of the bulk quality. In Hooge's equation [7], the noise magnitude is modeled as a linear function of $1/f$, and the proportionality constant is influenced by the material bulk quality. Kleinpenning [8] had extended the noise model to devices inclusive of diodes and solar cells with the equation

$$SI = \alpha q I/(f\tau) \qquad (1)$$

where I is the forward current, q is the elementary charge, τ is the dominant recombination lifetime, and α is the parameter reflecting the bulk quality. It is known that defects such as electron traps and dislocations lead to higher α and lower τ, thus increasing the $1/f$ noise.

Defects also contribute to excessive noises in the form of $1/f^\delta$, producing noise spectra of high magnitude and gradient, as explained by McWhorter [8] and other recent studies [9]–[13]. Additionally, Vandamme *et al.* [11] had shown that the presence of iron contaminants and interstitial oxygen reduced minority carrier lifetime of n^+p diodes and increased the devices' $1/f$ noise. In another study by Bychikhin *et al.* [13], it had been shown that $1/f$ noise in GaN considerably increased with thermal aging due to a small increase in the value of the series resistance. All these suggested that $1/f$ noise is a very useful indicator for device reliability.

II. EXPERIMENT

This paper studies the effects of ZnO nanorod growth time and dye-loading time on the photoconversion efficiency of the ZnO DSSC and examines the LFN as the two parameters vary. For this, DSSCs of 2.25 cm^2 in size were fabricated by precipitation growth of ZnO on an indium-doped tin oxide (ITO) glass. This was done by dropping a ZnO nanoparticle solution onto the ITO glass and air dried to form the ZnO seed layer. The seeded substrates were then immersed in a zinc

acetate solution added with ammonia for the growth of ZnO nanorods over 21–28 h. Thereafter, the samples were washed with deionized water and annealed in air at 450 °C for 30 min. The samples were then immersed into a ruthenium dye solvent (N719) and placed into the oven at 50 °C for the required durations. A batch of samples with varying ZnO growth times of 21–28 h was dye sensitized for 60 min for analyzing the growth time effect. Another batch with equal ZnO growth time of 25 h was dye loaded over a different duration of 20–70 min for analyzing the effect of loading time on dye adsorption.

The DSSCs were completed by encapsulating a thin layer of electrolyte in between the dye-sensitized ZnO and a platinum-coated ITO glass. The electrolyte consisted of 3-hexyl-1-methylimidazolium iodide (HMII), iodine, lithium iodide, and 4-tert-butylpyridine in methoxypropionitrile. The samples were characterized under a calibrated AM 1.5G solar simulator of 100 mW/cm^2. The current–voltage $(I–V)$ curves were obtained on a source meter (Keithley 2420) and consolidated on a computer for photoconversion efficiency analysis. To obtain the noise spectral, the photocurrent generated by the samples under the same simulated light source was amplified by a low-noise preamplifier (SR560) and subsequently processed by a dynamic signal analyzer (HP 35670) and analyzed on a computer.

III. RESULTS AND ANALYSIS

To verify the effects of growth time, the scanning electron microscope images of the ZnO nanorods were studied. It was noted that the nanorods rapidly grew for the beginning 26 h, and after which, the growth declined and almost stopped upon reaching a saturated length of approximately 2 μm. This was expected due to depletion of the precursors for ZnO growth and the growth-limiting effects imposed by the randomly oriented surrounding nanorods. The sheet resistance of the ITO surface was also monitored during the growth period and found to have increased from 13.60 Ω/sq at 21 h to 13.89 and 14.23 Ω/sq at 26 and 28 h, respectively. This proved that the ITO–ZnO interface had deteriorated under prolonged ZnO growth time.

The efficiency extracted from the $I–V$ curve and the short-circuit current increased with growth time during the 21st–24th hours, and after which, it declined (Fig. 1). The initial increase in the efficiency and short-circuit current corresponded with the increasing nanorod growth length during the same period. As the nanorods assumed a higher aspect ratio, the photoactive surface was drastically enlarged. The longer growth time also increased ZnO coverage on the underlying ITO electrode film and prevented the iodide electrolyte from corroding the ZnO–ITO interface.

The subsequent decline in the efficiency and short-circuit current was likely to be the results of structural defects developed as the nanorods stopped growing upon the depletion of growth precursors while yet subjecting to dissolution effects from the growth solution. Prolonged immersion in the growth solution corroded the ZnO–ITO interface, giving rise to interfacial defects. Such phenomena were acknowledged by researchers, including Liu and Aydil [4]. These defects served as electron traps and reduced the photocurrent injection efficiency.
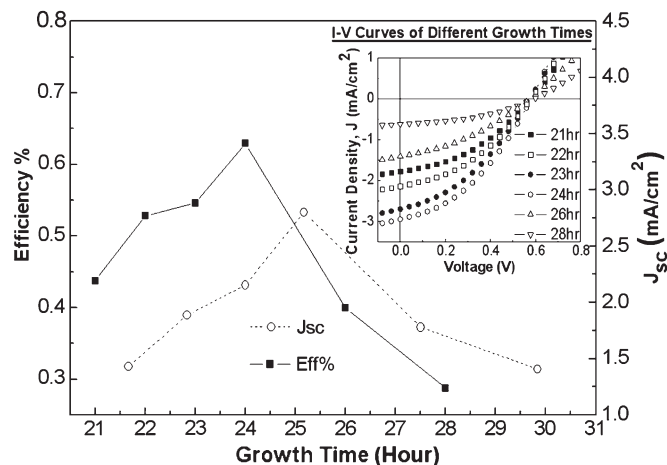

Fig. 1. Efficiency and J_{SC} of samples (sensitized for 60 min) versus growth times. (Inset) $I–V$ characteristics graph for different growth times.
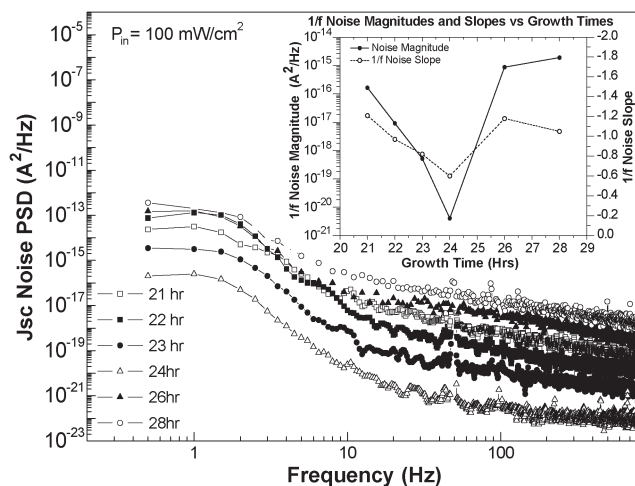

Fig. 2. LFN spectral of different samples of different growth times. (Inset) Noise power spectral densities (PSDs) and slopes extracted from the linear regression lines fitted between 30 and 800 Hz.

The noise spectral of samples of different growth times were exhibited in Fig. 2, and it could be observed that the spectral assumed a $1/f$ profile between 30 and 800 Hz. Linear regression lines were fitted on each spectral (in logarithmic scale) between 30 and 800 Hz. Thus, the gradient of the regression lines represents the noise gradient, whereas the y-intercepts represent the noise magnitude at 1 Hz.

The noise magnitude decreased with the ZnO growth time from the 21st to the 24th hour, as opposed to the trend of the efficiency and short-circuit current during the same period. This could be explained by (1) that the reduction in α and the rise in τ exert a more dominant effect than the rise in the photocurrent. The changes in α and τ were likely due to longer growth duration, leading to higher ZnO bulk quality, stronger ZnO–ITO interfacial bond, and more complete coverage of ZnO on the anode film. These improvements also reduced excess $1/f^\delta$ noises, leading to a reduction of the noise gradient (see Fig. 2, inset).

Under extended growth time, the noise magnitude and gradient trended higher. This was likely due to similar factors that reduced device efficiency, namely, structural defects in the nanorod bulk layer and ZnO–ITO interface, and weaker
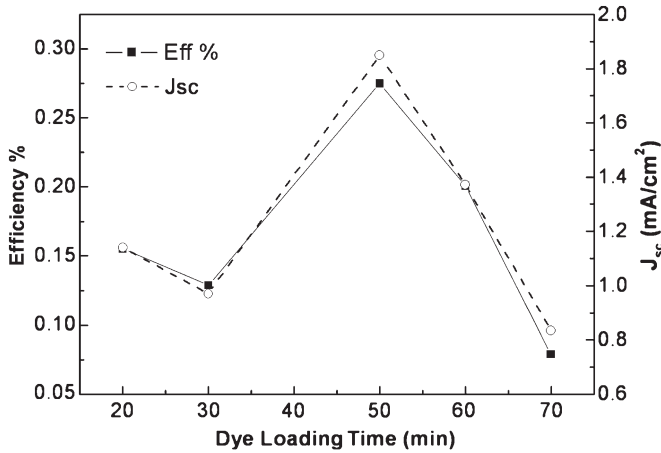
Fig. 3. Efficiency and J_{SC} of the samples (growth time of 25 h) versus dye-loading times.
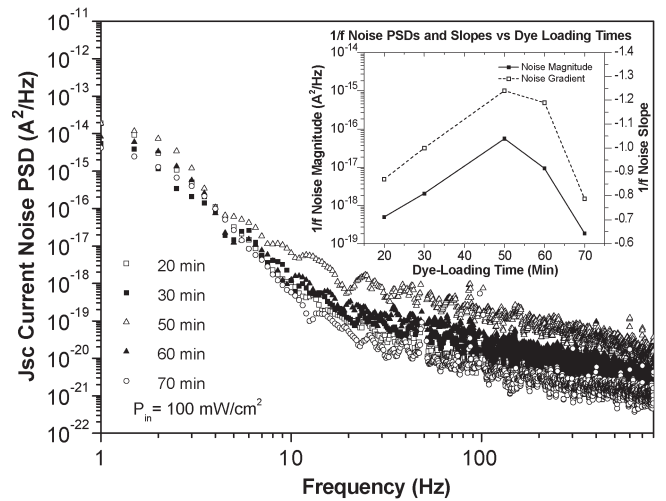

Fig. 4. LFN spectral of samples with different dye-loading times. (Inset) Plot of noise PSDs and slopes extracted from the linear regression lines fitted between 30 and 800 Hz.

ZnO–ITO bond. These defects act as electron traps and reduced the carrier recombination lifetime τ. Moreover, a lower ZnO bulk quality increased α and resulted in a higher noise magnitude. The defects also produced excessive noises thus, contributing to a higher noise gradient.

The efficiency of the sample increased with the dye-loading time and reached the maximum at an optimum loading duration of 50 min and then rapidly declined (Fig. 3). The initial rise in the efficiency with time is expected because more dye diffused into the ZnO layer to cover a larger area for solar excitation. After the nanorods were completely covered, however, further dye loading would not improve the efficiency as only the dye adsorbed directly onto the nanorods surface could inject electrons and contribute to the photocurrent. As the dye-loading time was extended, the efficiency was observed to rapidly drop. This could be due to undesirable shielding effects from the extra dye and agglomeration of the dye to form Zn^{2+}/dye complex on the ZnO surface. Dye agglomeration is significant in the ZnO DSSC due to poor chemical stability of ZnO in an acidic dye solution.

The noise spectral of each sample of different dye-loading times is exhibited in Fig. 4, and it was again observed that the spectral largely followed a $1/f$ profile between 30 and 800 Hz. A linear regression line was fitted on each spectral at this frequency range to extract the gradient and magnitude of the $1/f$ noise. It could be seen that the noise magnitude increased with the dye-loading time in the initial phase of 20–50 min, which was in line with the efficiency and short-circuit current in the same period. This could again be explained with (1), which related the $1/f$ noise magnitude as a linear function of current. As the dye-loading time increased, the ZnO dye covered a larger area and increased the photocurrent, which rendered the noise magnitude larger. It is further noted that the noise gradient decreased with time during the initial dye-loading period (inset in Fig. 4), which implied a reduction in the excessive noises due to stronger dye anchorage on the nanorod surface when given sufficient loading times for dye loading.

In the analysis of dye-loading time, the noise magnitude and gradient followed the trend of the short-circuit current, as opposed to the observation discussed in the analysis of

ZnO growth time. In the samples for dye-loading analysis, the change in current was likely to exert a more dominant effect than α and τ in Kleinpenning's noise equation. This is understandable as the comparison was performed on samples with equal growth time of 25 h and presumably with similar growth length, as well as bulk and interfacial quality. The changes in α and τ due to differing dye-loading time were likely to be small, but the effects were still observable as the shift in the noise gradients.

As the dye-loading time exceeded the optimum point of 50 min, the noise magnitude drastically declined. This was likely to be due to the same reasons that caused the drop in the efficiency and photocurrent as discussed earlier, namely, the shielding effects from extra dye molecules and agglomeration of the dye. The noise gradient sharply decreased as the dye-loading time was stretched to 70 min, and this was likely due to the decline in generation–recombination activities as the device efficiency dropped.

IV. CONCLUSION

The experiment has explained the mechanisms of nanorod growth and dye sensitizing in the ZnO-based DSSC and accounted for the influences of the time durations of the two processes on the efficiency. The LFN had shown to be reflective of the device quality changes induced by the growth and sensitizing mechanisms. This highlights the usefulness of the LFN in monitoring and optimizing process parameters in DSSC fabrication.

REFERENCES

[1] B. O'Regan and M. Grätzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO$_2$ films," *Nature*, vol. 353, no. 6346, pp. 737–740, Oct. 24, 1991.

[2] J. B. Baxter, A. M. Walker, K. van Ommering, and E. S. Aydil, "Synthesis and characterization of ZnO nanowires and their integration into dye-sensitized solar cells," *Nanotechnology*, vol. 17, no. 11, pp. S304–S312, May 2006.

[3] K. Keis, J. Lindgren, S.-E. Lindquist, and A. Hagfeldt, "Studies of the adsorption process of Ru complexes in nanoporous ZnO electrode," *Langmuir*, vol. 16, no. 10, pp. 4688–4694, 2000.

[4] B. Liu and E. S. Aydil, "Growth of oriented single-crystalline rutile TiO_2 nanorods on transparent conducting substrates for dye-sensitized solar cells," *J. Amer. Chem. Soc.*, vol. 131, no. 11, pp. 3985–3990, Feb. 2009.

[5] A. D. Pasquier, H. Chen, and Y. Lu, "Dye sensitized solar cells using well-aligned zinc oxide nanotip arrays," *Appl. Phys. Lett.*, vol. 89, no. 25, p. 253 513, Dec. 2006.

[6] T. P. Chou, Q. Zhang, and G. Cao, "Effects of dye loading conditions on the energy conversion efficiency of ZnO and TiO_2 dye-sensitized solar cell," *J. Phys. Chem. C*, vol. 111, no. 50, pp. 18 804–18 811, Nov. 2007.

[7] F. N. Hooge, " $1/f$ noise sources," *IEEE Trans. Electron Devices*, vol. 41, no. 11, pp. 1926–1935, Nov. 1994.

[8] L. K. J. Vandamme, "Noise as a diagnostic tool for quality and reliability of electronic devices," *IEEE Trans. Electron Devices*, vol. 41, no. 11, pp. 2176–2187, Nov. 1994.

[9] L. Ke, X. Y. Zhao, R. S. Kumar, and S. J. Chua, "Low-frequency noise measurement and analysis in organic light-emitting diodes," *IEEE Electron Device Lett.*, vol. 27, no. 7, pp. 555–557, Jul. 2008.

[10] L. Ke, R. S. Kumar, and C. Vijila, "Correlation of current noise behavior and dark spot formation in organic light-emitting diodes," *IEEE Electron Device Lett.*, vol. 29, no. 1, pp. 67–69, Jan. 2008.

[11] L. K. J. Vandamme, E. P. Vandamme, and J. J. Dobbelsteen, "Impact of silicon substrate, iron contamination and perimeter on saturation current and noise in n^+p diodes," *Solid State Electron.*, vol. 41, no. 6, pp. 901–908, Jun. 1997.

[12] J. L. Herve, L. K. J Vandamme, and P. W. M Blom, "Low-frequency noise in polymer light-emitting diodes," in *Proc. 14th ICNF*, C. Claeys and E. Simoen, Eds., 1997, pp. 508–511.

[13] S. Bychikhin, L. K. J. Vandamme, G. Meneghesso, E. Zanoni, and D. Pogany, "Low-frequency noise sources in as-prepared and aged GaN-based light-emitting diodes," *J. Appl. Phys.*, vol. 97, no. 12, pp. 123 714-1–123 714-7, Jun. 2005.

Szu Cheng Lai received the B.S. degree in electrical and electronic engineering from the National University of Singapore, Singapore, in 1999.

He is currently a Senior Research Officer with the Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research (A*STAR), Singapore. He has more 10 years of experience in electronics design and nanotechnology research. During his R&D career at IMRE, he has successfully designed and developed products and application platforms for various technologies generated by the research institute. He has contributed more than 10 publications related to the field of science and engineering. He is the holder of five patents.
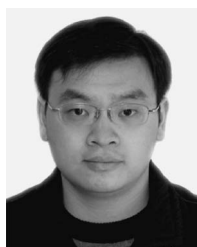
Ming Fei Yang was born in Chongqing, China. He received the B.Eng. degree (with first-class honors) in microelectronics in 2008 from Nanyang Technological University, Singapore, where he is currently working toward the Ph.D. degree in microelectronics.

His research mainly focuses on the optimization of semiconductor thin films (e.g., Si and Ge) and their device applications.

Surani Bin Dolmanan received the B.Sc. (with honors) and M.Sc. degrees in material science and engineering from the National University of Singapore, Singapore, in 1999 and 2007, respectively.

He has seven years of experience in thin-film processing, integration, and technology development. He was a Senior Engineer with the Systems on Silicon Manufacturing Company (SSMC), Singapore, where he worked on process development and optimization of silicon wafer processing at various technology nodes. He was also involved in various technology transfer activities between SSMC, Taiwan Semiconductor Manufacturing Company (TSMC), Taiwan, and Philips Semiconductor, Netherlands. He is currently with the Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A*STAR), Singapore, where he is involved in R&D and has been working on fabrication and electrical and optical characterization of GaN LEDs and organic devices to facilitate the institute's research programs in nanotechnology and material science.

Lin Ke received the Ph.D. degree from the National University of Singapore, Singapore, in 2004.

She has more than ten years of experience in the field of electronic device research, currently as the Project Leader with the Institute of Material and Research Engineering, Agency for Science, Technology and Research (A*STAR), Singapore. She has 42 international journal publications and 25 oral conference presentations and invited talks. She is the holder of five patents. Her main research interests include organic electronics, optoelectronics, organic light-emitting diodes, organic thin-film field-effect transistors, photovoltaic device physics, degradation and applications, noise analysis, device optical/electrical characterization, and display evaluation.

Xiao Wei Sun (SM'06) was born in Beijing, China. He received the B.Eng., M.Eng., and Ph.D. degrees in photonics from Tianjin University, Tianjin, China, in 1990, 1992, and 1996, respectively, and the Ph.D. degree in electrical and electronic engineering from the Hong Kong University of Science and Technology, Kowloon, Hong Kong, in 1998.

Since 1998, he has been with the Division of Microelectronics, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, first as an Assistant Professor, and was promoted to Associate Professor in 2005. His research interests focus on MOCVD growth of ZnO, display technologies, and nanotechnology.

Dr. Sun is a Fellow of the Institute of Physics and a member of the Society for Information Display (SID). He is the Founding Chair of SID Singapore and Malaysia Chapter. He was the recipient of the Nanyang Award for Research and Innovation in 2009.