Influence of silicon texturization on the photovoltaic properties of CuPc/n-Si hybrid solar cells

Zhifeng Liu¹, a, YiTing Liu², b
¹NO.114 Nanta Street, Shenyang, 110016 P.R.China
²School of physics and optoelectronic technology, Dalian University of Technology, Dalian, P.R.China

a liuzhifeng@sia.cn, b liuyiting713823@yahoo.com.cn

Key words: Hybrid solar cell, Copper phthalocyanine, Textured Si

Abstract. Hybrid solar cell based on copper-phthalocyanine (CuPc) and textured Si has been fabricated. Influence of silicon texturization on the photovoltaic properties of CuPc/n-Si hybrid solar cell was studied by current-voltage characteristic curves in the dark and under illumination conditions. As a result, it is found that textured Si can improve significantly the performance of hybrid solar cell. It exhibits a three times increase in the short-circuit current density with respect to that of the standard hybrid solar cell, and the short-circuit current density reaches up to 5.4 mA/cm². In addition, the open-voltage and fill factor are almost constant. The solar-energy conversion efficiency is increased by about three times by the textured Si and achieved about 0.8% under “one Sun” illumination. Furthermore, the possible reasons for this result have been discussed.

Introduction

The search for low cost alternatives to inorganic semiconductors resulted in a growing interest in organic materials [1]. In addition, hybrid organic/inorganic structures seem to offer a viable solution for solar cells due to utilizing the large carrier mobility in inorganic materials and the strong photo-absorption coefficient in organic materials. Inorganic semiconductors and some of organic ones have been studied well. Therefore, it may be possible to easily find an optimal combination of two kinds of semiconductor materials in order to improve the solar cell’s performance. Copper phthalocyanine (CuPc) has been proposed for numerous applications including organic light-emitting diodes [2] and photovoltaic cells [3-6] due to its high thermal and chemical stability and excellent optoelectronic properties. CuPc-based hybrid solar cells have been the focus of intense research in recent years [7, 8]. However, they continue to suffer from low solar-energy conversion efficiency [9]. Furthermore, the CuPc-based solar cells behavior is not as well understood as in case of inorganic solar cells and further research is still going on.

Surface texturization process of inorganic semiconductor materials may reduce optical reflectance and enhance effective light absorption [10, 11]. It has been shown to be an effective way to enhance the photovoltaic conversion efficiency in inorganic solar cells [12]. However, it has been seldom used in inorganic-organic hybrid solar cells.

The present investigation explores the possibility of improving the solar cell based on hybrid organic–inorganic structure. In this paper, Au/CuPc/n-Si/Al hybrid solar cells were fabricated, and theirs optical and electrical properties were analyzed. Influence of silicon texturization on the photovoltaic properties of CuPc/n-Si solar cells was studied, and the possible reasons for this result were discussed. Experimental and theoretical basis for the future to further improve the photoelectric conversion efficiency of the CuPc/n-Si hybrid solar cells has been provided.

Experimental Details

For the solar cell fabrication, phosphorous doped <100> oriented single crystal n-type Si wafer with a resistivity of 50 mΩ·cm was used as substrate. They were thoroughly cleaned in an ultrasonic bath with acetone, ethanol and de-ionized water successively, and then were dipped in 5% HF solution
to remove the natural oxide from the surface. Substrates with randomly distributed upside pyramids were prepared by anisotropic etching of Si using a low concentrated alkaline-isopropanol solution. In our experiment, an alkaline solution of sodium hydroxide (NaOH) and isopropyl alcohol (IPA) was adopted as etchant. The substrates were first dipped into the etchant solution at 95 °C for 25 min, and then rinsed twice in distilled water. In order to eliminate the traces of water, all substrates were dried by blowing nitrogen gas. The back side of a Si wafer was treated with HF solution to remove SiO₂ followed by evaporating Al to form an Ohmic contact. CuPc, purchased from Aldrich Chemical Co. (with a purity of 99%), was used without further sublimation. Unlike usual method of copper-phthalocyanine film fabrication, the thin film was grown by spin coating from saturated chlorobenzene solution in this paper. The thin film was dried for 12 h to evaporate the solvent. The gold electrode was deposited by thermal evaporation in a vacuum chamber (2×10⁻³ Pa) through a shadow mask, resulting in multiple devices. The 0.1 cm² active cell area was used for the present investigation. Fig.1 shows the configuration of the basic experimental device (a) and the molecular structure of CuPc used as an organic semiconductor (b).

![Fig. 1 The configuration of the basic experimental device (a) and the molecular structure of CuPc](image)

The morphology and dimension of the alkaline solution treated Si substrate was observed by field-emission scanning electron microscopy (FESEM) on HITACHI S-4800. The surface reflectivity of silicon wafers before and after the etching process was measured. The reflectance measurement setup consisted in a spectrophotometer and an integrating sphere. Electrical characterization was performed with a potentiostat/Galvanostat electrochemical analyzer (Model 263A) in the dark and under the illumination of a simulated solar light (AM1.5) with 100 mW/cm². All measurements were performed in ambient air at room temperature.

**Results and Discussion**

**Scanning Electron Microscopy.** In order to improve the conversion efficiency of the solar cells, it is very important to reduce optical reflectance and enhance effective light absorption. Efficient suppression of optical reflection in a broad spectral range has been achieved by deep surface texturing. Rough surfaces with spikes and pits having typical sizes of several micrometers exhibit a reduced reflectivity due to the multiple reflection and absorption. It is well known that the surface of (100) mono-crystalline silicon wafers with alkaline etching can form randomly distributed upside pyramids, which can effectively enhance light absorption. When mono-crystalline silicon wafers are put in alkaline solution at a certain temperature, the etch rate is different on the different orientation due to the discrepancy of silicon atom array spacing on different orientation. By using lowly concentrated alkaline solution in highly etched temperature, the discrepancy of the etch rate between the <100> direction and the <111> direction is obvious. The ratio of the etch rate is called as anisotropy factor (AF). The anisotropy etching process by changing the concentration and temperature of the alkaline solution can effectively change AF, which lead to the etch rate in the <111> direction is very low compared to the etch rate in the <100> direction. So that the surface of
silicon wafers can form randomly distributed upside pyramids, called as light trapping structures [13]. The structures can effectively reduce the reflection loss from the front surface [14] and enhance the light absorption, so that improve the conversion efficiency of the solar cells.

The surface morphology of the alkaline solution treated Si substrate has been studied through scanning electron microscopy (SEM). Randomly distributed pyramid structures were formed on the surface of Si wafer, as shown in Fig. 2(a). The initial surface orientation of Si<100> substrate changes to Si<111> orientation on the pyramid facets during the anisotropic etching process. It reveals relatively smooth surfaces over large areas covered with different size of pyramids. The cross-sectional view of the sample was shown in Fig. 2(b). As the picture show, the pyramids have grown in size with larger duration of texturization and have become regular and more uniformly distributed. The average pyramid base size is between 2 and 6 µm.

Reflectance Spectrum. The quality of surface texturization can be reflected directly by the surface reflectivity. Low reflectivity means that the light absorption increase, and hence the opportunity to generate the carriers also increase. The reflectance curves of silicon wafers before and after the etching process were shown in Fig.3. The reflectance of untextured silicon wafer is very high. The average reflectance is 40.7%. However, after the etching process, the surface reflectance of silicon wafer has been significantly reduced. The average reflectance is reduced to 18.9%. The decrease of reflectance is obvious, especially in the wavelength range from 500 to 1000 nm, the reflectance is below 20% and the lowest 14%. It indicates that using an alkaline solution of sodium hydroxide and isopropyl alcohol to etch silicon wafer can effectively reduce the surface reflectance.
**Current-Voltage Characteristics.** The Current-Voltage (I-V) characteristics of Au/CuPc/n-Si/Al (a) and Au/CuPc/textured n-Si/Al (b) hybrid solar cells in the dark and under “one Sun” illumination conditions were shown in Fig. 4. Dark I-V measurements showed good rectifying behavior for both the solar cells. Under forward bias, there is a photovoltaic effect in each figure. For the standard solar cell, an open-circuit voltage ($V_{oc}$) of 270 mV is observed. However, the device exhibited a high fill factor (FF) of 65% and a relatively low short-circuit current density ($J_{sc}$) of 1.29 mA/cm$^2$. It is thought that in this device, both FF and $J_{sc}$ are series-resistance limited. The solar cell with the alkali solution treated Si substrate gave $V_{oc} = 260$ mV and $J_{sc} = 5.4$ mA/cm$^2$. Thus a substantial increase in $J_{sc}$ (from 1.29 to 5.4 mA/cm$^2$) was obtained even though a $J_{sc}$ value of 5.4 mA/cm$^2$ is still too low. The device exhibited a high fill factor of 71%. Calculated by the formula of the photoelectric conversion efficiency of solar cells, the solar-energy conversion efficiency is increased by about three times by the textured Si and achieved about 0.8% under “one Sun” illumination.

![Current-Voltage Characteristics](image)

**Fig. 4** The current-voltage plot for Au/CuPc/n-Si/Al (a) and Au/CuPc/textured n-Si/Al (b) hybrid solar cells in the dark and under illumination conditions.

Here, photoelectric conversion efficiency of solar cell is mainly attributed to the increase in short-circuit current. An important feature of this solar cell structure is a surface textured Si that is introduced to increase the light absorption, and hence the short-circuit current, in two ways: (1) by a reduction of the reflection loss at the Si/CuPc interface that on account of its roughness with sub-wavelength lateral structures produces a graded index of refraction, this effect applies to practically the whole spectral range of the incident light;
(2) by changing the incident light in the forward direction of the crystalline bulk Si, which not only to extend the optical path and thus result in an increase of light absorption, but also to increase the number of photons and generate more photo-generated carriers near the p-n junction, thereby the probability of photo-carrier collection is enhanced.

In addition, a surface textured Si can increase the contact area of the p-type and n-type material, that is, the p-n junction area. The separation of electron-hole pairs at the CuPc/Si interface is enhanced, and hence the short-circuit current increased.

Conclusions
Copper-phthalocyanine and n-Si hybrid solar cell has been fabricated by combining with spin coating and anisotropy etching processes. Current-voltage characteristic curves in the dark and under illumination conditions were used to analyze solar cells performance. As a result, it is found that textured Si can improve significantly the performance of hybrid solar cell. It exhibits a three times increase in the short-circuit current density with respect to that of the standard hybrid solar cell, and the short-circuit current density reaches up to 5.4 mA/cm². In addition, the solar-energy conversion efficiency is increased by about three times by the textured Si and achieved about 0.8%. This experiment showed that the silicon texturization provides an effective way to improve the performance of CuPc/n-Si hybrid solar cells.

Acknowledgements
This work is supported by the National High Technology Research and Development Program of China (863 Program). The project number is 2011AA040102.

References
[1] D.T. Zahn, M. Gorgoi and O.D. Gordan: Solar Energy, Vol. 80 (2006) No.6, p.707.
[2] H. Aziz, Z.D. Popovic, N.X. Hu, Ah-Mee Hor and G. Xu: Science, Vol. 283 (1999), p.1900.
[3] P. Peumans, A. Yakimov and S.R. Forrest: Journal of Applied Physics, Vol. 93 (2003) No.12, p.3693.
[4] C.W. Tang: Applied Physics Letters, Vol. 48 (1986) No.2, p.183.
[5] P. Peumans, V. Bulovic and S.R. Forrest: Applied Physics Letters, Vol. 76 (2000) No.19, p.2650.
[6] A. Yakimov and S.R. Forrest: Applied Physics Letters, Vol. 80 (2002), p.1667.
[7] G.D. Sharma, Raj Kumar, Shailendra Kumar Sharma, and M.S. Roy: Solar Energy Material and Solar Cells, Vol. 90 (2006) No.7-8, p.933.
[8] R. Prabakaran, E. Fortunato, R. Martins, and I. Ferreira: Journal of Non-Crystalline Solids, Vol. 354 (2008) No.19-25, p.2892.
[9] I. A. Levitsky, W. B. Euler, N. Tokranova, B. Xu, and J. Castracane: Applied Physics Letters, Vol. 85 (2004) No.25, p.6245.
[10] V. Pierre, E. Olivier, M.Emmanuel and AndréCrahay: Solar Energy Material and Solar Cells, Vol. 26 (1992) No.1-2, p.71.
[11] E. Vazsonyi, K.D. Clercq, R. Einhaus, E. Van. Kerschaver, K. Said, J. Poortmans, J. Szlučík and J. Nijs: Solar Energy Material and Solar Cells, Vol. 57 (1999) No.2, p.179.
[12] E.S.Rittner and R.A. Arndt: Journal of Applied Physics., Vol. 47 (1976) No.7, p.2999.
[13] H. Angermann, J. Rappich, L. Korte, I. Sieber, E. Conrad, M. Schmidt, K. Hubener, J. Polte and J. Hauschild: Applied Surface Science, Vol. 254 (2008) No.12, p.3615.
[14] J. Szlučík, S. Sivoththaman, J.F. Nijs, R.P. Mertens and R. Van Overstraeten: Proceedings of the IEEE, Vol. 85 (1984), p.711.