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Effective Light Trapping in Thin Film Silicon Solar Cells with Nano- and Microscale Structures on Glass Substrate

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For thin film silicon-based solar cells, effective light trapping at a broad range of wavelengths (400–1100 nm) is necessary. Normally, etching is only carried out with TCOs, such as SnO_2:F and impurity doped ZnO, to form nano-sized craters in the surface morphology to confer a light trapping effect. However, in this study, prior to ZnO:Al etching, periodic structures on the glass substrates were made by photolithography and wet etching to increase the light scattering and internal reflection. The use of periodic structures on the glass substrate resulted in higher haze ratios in the range from 550 nm to 1100 nm, which is the optical absorption wavelength region for thin film silicon solar cells, than obtained by simple ZnO:Al etching. The periodically textured glass with micro-sized structures compensates for the low haze ratio at the middle and long wavelengths of wet etched ZnO:Al. ZnO:Al was deposited on the periodically textured glass, after which the ZnO:Al surface was also etched randomly using a mixed acid solution to form nano-sized craters. The thin film silicon solar cells with 350-nm-thick amorphous silicon absorber layer deposited on the periodic structured glass and etched ZnO:Al generated up to 10.68% more photocurrent, with 11.2% increase of the conversion efficiency compared to the cell deposited on flat glass and etched ZnO:Al.

Keywords: Light Trapping, Chemically Etched Textures, AZO, Thin Film Silicon Solar Cell.

1. INTRODUCTION

In thin film silicon solar cells, hydrogenated amorphous silicon (a-Si:H) and/or microcrystalline silicon (μm-Si:H) are used as an absorption layer. For the effective absorption of incident light by the solar cells, light management through texturing of the surface on which the light is incident is necessary. Introduction of surface texture can result in enhanced scattering and internal reflection of the incoming light in solar cells.[1] Texturing increases the optical path, resulting in distinct increases in the photocurrent and quantum efficiency.

Surface morphology, which can be obtained by etching processes, allows more scattering and reflection at rough internal interfaces, leading to more efficient light trapping and subsequent increase of the light absorption in cells.[2] Generally, surface texturing is carried out on the transparent conductive oxide layer (TCO) of superstrate-type thin film silicon solar cells.[3–5] Although chemically etched ZnO:Al deposited by the commercial sputtering process shows excellent light trapping properties, it is only effective for short wavelengths, with rapid decrease of effectiveness at longer wavelengths. Thus, better light scattering and internal reflection in the infra-red region must be obtained to supplement the loss.

To achieve good light trapping through etching, the feature size of the structures on the surface must be considered, since small-sized structures (hundreds of nm) have scattering effects in the short wavelength region, while large-sized structures (several μm) have scattering effects in the long wavelength region.[6] Recently, multiple surface

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texture technologies, such as doubly textured TCO and etched TCO on textured substrate, have been studied.[6,7] Different-sized structures are formed by etching on multiple surfaces to achieve effective light management.[8,9] Since the thin film solar cell was deposited on the substrate, its shape followed the substrate resulting in better scattering effect.

In the present study, the glass substrate was periodically textured to allow good light trapping at long wavelengths, after which ZnO:Al film was deposited on the glass. The texture of the sputtered ZnO:Al film was then controlled by a chemical etching step in diluted complex acid for effective light trapping at shorter wavelengths.

2. EXPERIMENTAL DETAILS

The complete process of ZnO:Al texturing on the glass substrate is schematically illustrated in Figure 1. For the glass substrate, Corning Eagle 2000 glass was used. Before use, it was ultrasonically cleaned in acetone, isopropyl alcohol and deionized water for 10 min each, and then dried with an N_2 spray gun. To make periodic structures on the glass substrate, photolithography was carried out, and hydrofluoric (HF) acid was used to etch the glass. However, since the photoresist (AZ-7220) used during photolithography is easily lifted off by HF acids, the glass substrate must have a hard mask layer before the photolithography process. Therefore, silicon nitride (SiN_x) was employed herein as the hard mask, since it can withstand HF and can be easily removed by a reactive ion etcher (RIE). The photoresist was spin-coated on the hard mask to a thickness of 2 μm. The SiN_x not protected by the photoresist was then removed by RIE, which was carried out with 7 sccm of SF6 gas and the power of 20 W for 3 min. After formation of the hard mask pattern, the photoresist was removed by ultrasonic cleaning. The glass substrate with the mask pattern was then etched by dipping in diluted HF solution. The following equation is a simplification of the reactions occurring during the heterogeneous SiO_2 dissolution:[10]

$$SiO_2 + 6HF \rightarrow SiF_6^{2-} + 2H_2O + 2H^+ \tag{1}$$

To control the etching rate, the solution was diluted to 10% with deionized water. The temperature of the solution was maintained at 25 °C with a refrigerated bath circulator, WCR-P6. The deposition of 1 μm thick ZnO:Al films was then carried out with a 13.56 MHz radio frequency magnetron sputter system, using ZnO target with 2 wt% Al_2O_3. The chamber, which was equipped with a turbo-molecular pump, had a base pressure of 1.33×10^{-4} Pa. Fixed argon gas flow at 20 sccm was then flowed into the chamber through a mass flow controller. The r.f power during the ZnO:Al deposition was 225 W. The textured glass substrate was then cleaned with acetone, isopropyl, and de-ionized water for 10 min each by ultrasonic washing. The target was pre-sputtered for 10 min in order to remove contaminants.

The ZnO:Al deposited on the textured glass substrate was chemically wet etched in a mixture of oxalic acid ($C_2H_2O_4$), hydrochloric acid and DIW for 90 sec.[11] The temperature of the solution was maintained at 25 °C. The mixture solution consisted of 5 ml of hydrochloric acid (37%), 100 ml of oxalic acid (5.6%) and 295 ml of de-ionized water. The surface of the etched ZnO:Al layers exhibited U-shaped valleys with smooth craters. The surface topography and characteristic feature sizes were studied by scanning electron microscopy (SEM). The transmittance and diffused transmittance were also measured. For measurement of the optical properties of the textured ZnO:Al films, CH_2I_2 was used as an index-matching fluid to avoid systematic measurement errors due to the light scattering of the rough films.[12]

The p–i–n a-Si:H solar cells were prepared in a cluster-type plasma enhanced chemical vapor deposition (PECVD) system. After deposition of the a-Si:H solar cells, silver and aluminum electrodes were deposited in a separate vacuum chamber by evaporation. The complete device structure was glass/ZnO:Al (1 μm)/a-SiO_x (p) (30 nm)/a-Si:H (i) (350 nm)/a-Si:H (n) (40 nm)/Ag (200 nm)/Al (100 nm). The spectroscopic ellipsometry (VASE®, Woollam, 240 nm < λ < 1700 nm) was used to measure the film thickness, refractive index and optical absorption coefficient at an incidence angle of 65° in the spectral range of 240 to 1700 nm. To determine the effect of the surface morphology of the solar cells, the quantum efficiency (QE) of the a-Si:H solar cells was measured with a xenon lamp, monochromator and optical filters to filter out the high orders with a light probe beam impinging normal to the samples.

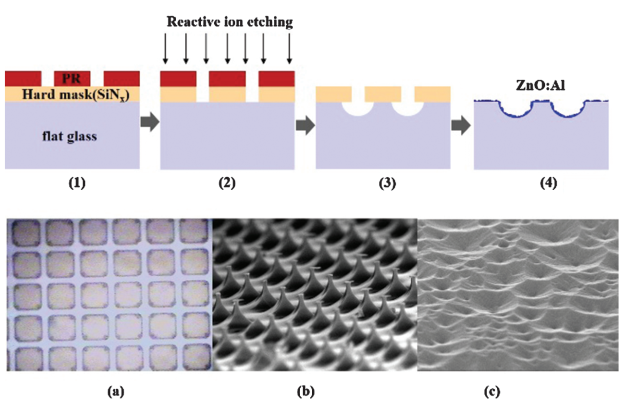


Figure 1. The first line (1–4) shows the process flow of the fabrication of doubly-textured substrate. The second line shows (a) an optical microscope image of the photoresist-patterned glass substrate, (b) an SEM image of the surface textured glass substrate, and (c) an SEM image of the etched ZnO:Al.

3. RESULTS AND DISCUSSION

Figure 2(a) shows cross-section views of the substrates with different glass etching times, taken by FE-SEM.

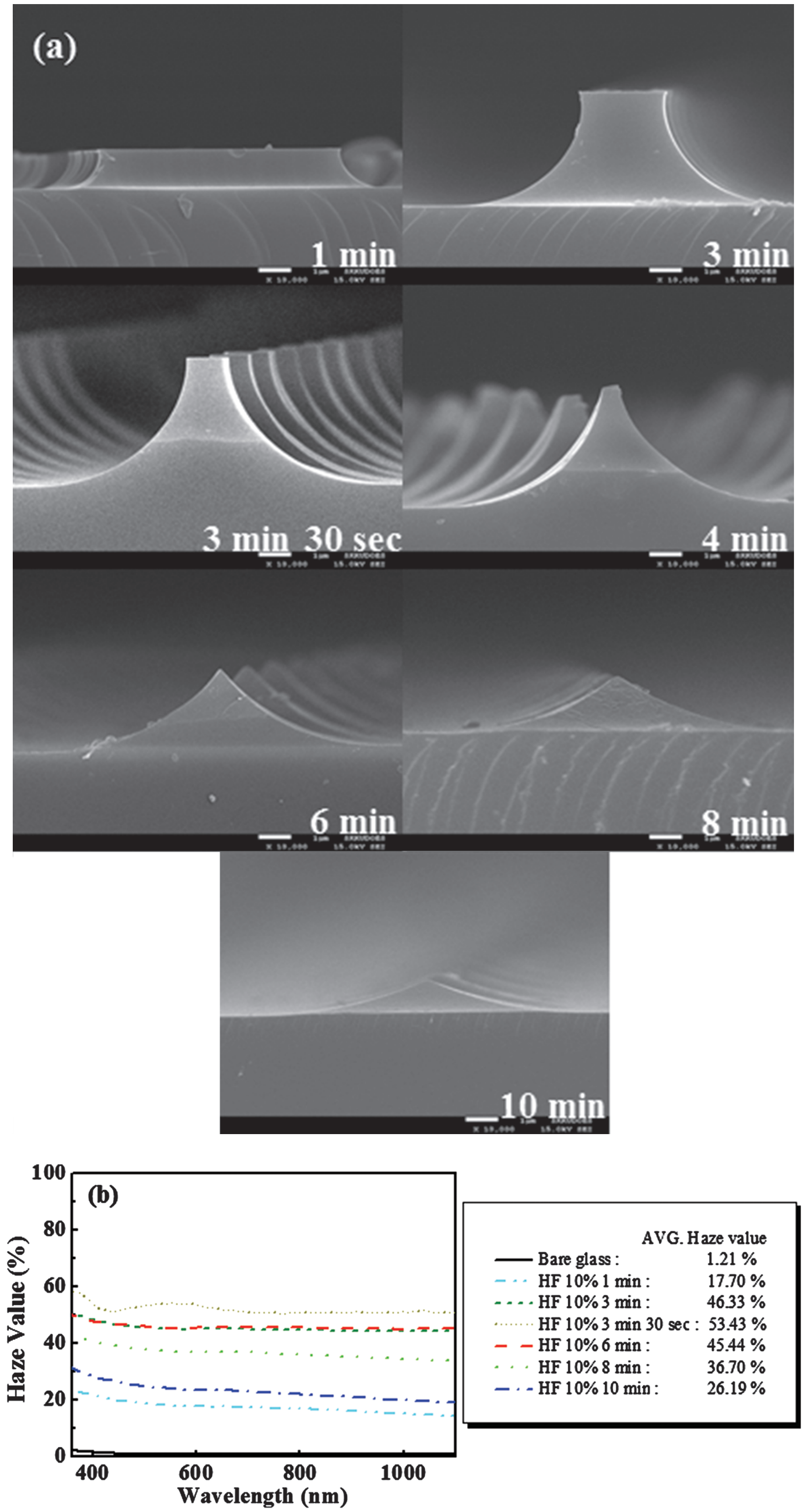


Figure 2. Characteristics of periodically textured glass substrate: (a) cross-sectional SEM image of textured glass substrate, and (b) haze values of textured glass substrate. It could be seen that the slopes were too steep when the etching time was not sufficient. Etching time of more than 6 min was required for stable *p*-layer deposition of the thin film solar cells.

The etching was carried out in the form of half-circles where no hard mask was present.

Uncovered glass surfaces were anisotropically etched out so that pyramid shapes remained on the glass substrate.

Figure 2(b) shows the haze values of the textured glass as a function of the etching time. The haze value was calculated from the following mathematical equation:

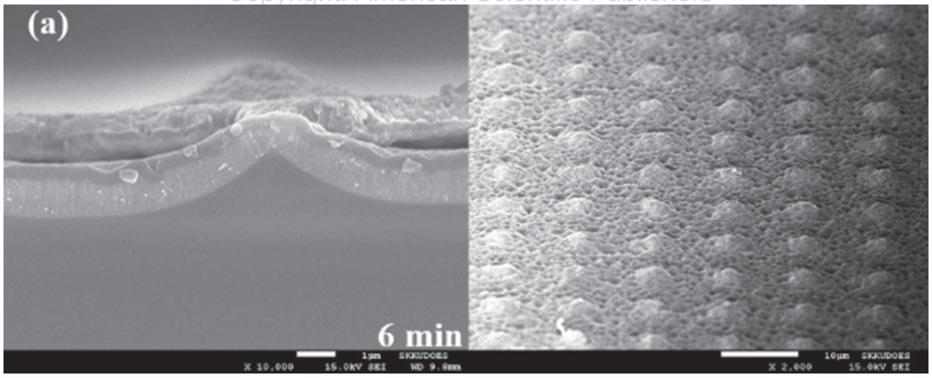
$$\text{Haze value} = \frac{T_{\text{Diffused}}}{T_{\text{Total}}} \times 100(\%) \qquad (2)$$

Where T_{Diffused} is the diffused transmittance and T_{Total} is the total transmittance.[13]

The haze values were proportional to the size of the structures. The haze value reached a peak for the sample etched for 3 min 30 sec, after which it started to decease again as the flat portion of the top got etched away. Since high haze value results in high short circuit current, it may seem that the samples etched for 3 min 30 sec to 4 min would be appropriate for the fabrication of solar cells. However, as it is mentioned above, the shape of the surface was unstable for deposition of several nm-thick *p*-layer by PECVD for samples etched less than 6 min. Therefore, the samples etched at least 6 min were used to fabricate the solar cells. For the solar cells, double texturing was used, i.e., ZnO:Al deposited on textured glass was etched again. As scattering does not occur in objects which are smaller than the wavelength of light, only the light at smaller wavelengths than the size of the craters gets scattered. Thus, ZnO:Al with craters several tens to hundreds of nano in size had high haze values only for the short wavelengths. The haze values of periodically textured glass substrate were almost the same throughout the absorption wavelength region, unlike those of chemically etched ZnO:Al. This is because light at wavelengths less than 1100 nm is scattered by glass substrates with structures of a few micrometers in size.[14]

Figure 3(a) shows SEM images of the cross-section and top view of the thin film silicon solar cell on a doubly textured substrate. It can be seen that the surface of the thin film solar cell retained the shape of the surface of the glass substrate and ZnO:Al. The surface resistance of ZnO:Al was 3.7 Ω/□ for flat glass and 4.7 Ω/□ for the sample with the glass etching time of 6 min. All samples exhibited values less than 6 Ω/□, which were suitable for thin film solar cell deposition. Figure 3(b) shows the haze values of the doubly textured surfaces. Craters several tens of nanometer to hundreds of nanometers in size were uniformly distributed on the etched ZnO:Al surface. The depth of the craters was a maximum of ~300 nm, and several-um-sized structures were not observed.

This explains the characteristic of the etched ZnO:Al, in which higher haze values were observed at short wavelengths than long wavelengths. The most notable trend was the change in haze values for the etched ZnO:Al on



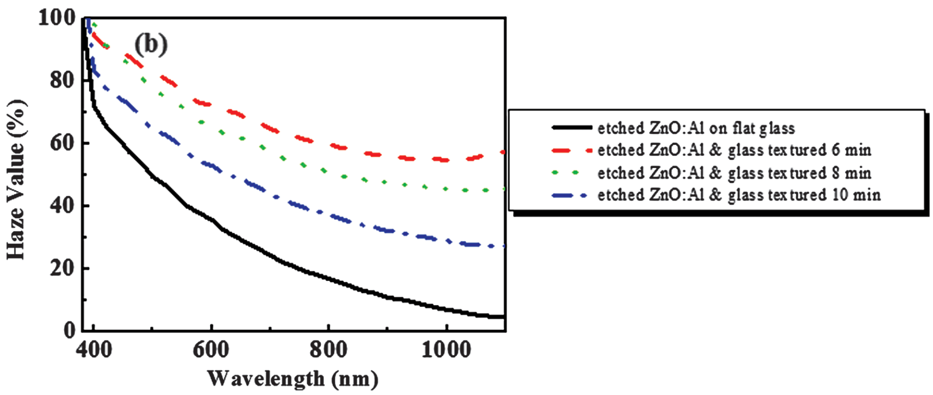


Figure 3. Characteristics of doubly-textured substrate: (a) SEM images of etched ZnO:Al on textured glass substrate, and (b) haze values of etched ZnO:Al on flat and textured glass.

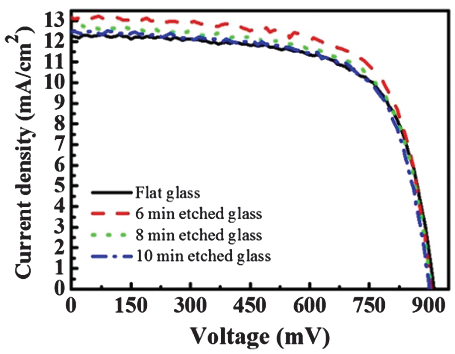


Figure 4. Current density versus voltage (J–V) characteristics of the a-Si:H thin film solar cells on doubly-textured substrates with different glass etching times.

textured glass. Compare to etched ZnO:Al on flat glass, the etched ZnO:Al on the textured glass displayed a dramatic increase of the haze value as the size of the structure on the glass became higher, especially in the long wavelength region.

To examine how the power conversion efficiency of the thin film solar cells could be improved by surface morphology, the J–V characteristics were measured under AM 1.5 at room temperature (25 °C). The J–V characteristics of the p–i–n thin film solar cells as a function of the etching time of the glass substrate are presented in Figure 4. For the case of the thin film silicon solar cells fabricated on flat glass, the short circuit current density (J_{sc}) was 11.89 mA/cm2. J_{sc} increased proportional to the size of the structures on the glass substrate. The best performance was obtained for the solar cell in which the substrate was etched for 6 min, displaying the V_{oc}, J_{sc}, FF and η values of 900 mV, 13.16 mA/cm2, 68.72% and 8.14%, respectively. The overall performance of the p–i–n thin film solar cells tested is summarized in Table I.

The increase of J_{sc} with the increase in haze values can be seen in the QE graph of Figure 5. As mentioned above, the haze value increased proportional to the size of the structure at short wavelengths, as well as long wavelengths. QE also increased throughout all wavelengths. A higher increase in QE was observed at the short wavelengths, especially 500 nm, since the haze value of the etched ZnO:Al and textured glass substrate was highest at the short wavelengths. In addition, the absorption wavelength of a-Si:H, which was used as an absorption layer,

Table I. The performance of p–i–n thin film solar cells on textured glass substrate as a function of the etching time.

Time (min)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	Eff. (%)
–	900	11.89	68.41	7.32
6	900	13.16	68.72	8.14
8	900	12.65	68.51	7.80
10	900	12.48	67.46	7.58

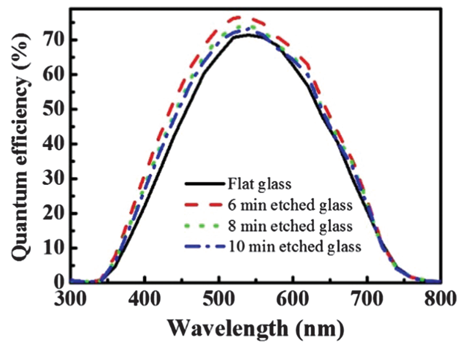


Figure 5. The Quantum Efficiency (QE) of a-Si:H thin film solar cells on doubly-textured substrate with different glass etching times.

was around 400~550 nm, and QE is more highly affected by the haze value at short wavelengths.

4. CONCLUSION

Periodically textured glass substrate and chemically etched ZnO:Al were employed to the single junction amorphous silicon solar cell to enhance the light trapping properties in the long wavelength region. The glass substrates were etched in diluted chemical solution for 6 min, 8 min and 10 min. The size of the structures obtained on the glass substrates was around 3 μm, and the haze values of the textured glass substrate in the long wavelength, from 550 to 1100 nm, were similar to those in the short wavelength. When the ZnO:Al deposited on the textured glass was etched, the haze values in the long wavelength were improved compared to those of the ZnO:Al deposited on flat glass. The best cell performance ($J_{sc} = 13.16$ mA/cm^2, FF = 68.72%, $V_{oc} = 900$ mV and $\eta = 8.14\%$) was obtained for the sample on textured glass etched for 6 min. The solar cell with the 6 min textured glass substrate also showed the highest quantum efficiency.

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References and Notes

1. D. Domińe, P. Buehlmann, J. Bailat, A. Billet, A. Feltrin, and C. Ballif, *Phys. Status Solidi Rapid Res. Lett.* 2, 163 **(2008)**.
2. P. Campbell, *J. Opt. Soc. Am. B* 10, 2410 **(1993)**.
3. J. I. Owen, W. Zhang, D. Köhl, and J. Hüpkes, *Journal of Crystal Growth* 344, 12 **(2012)**.
4. W. Zhang, E. Bunte, F. Ruske, D. Köhl, A. Besmehn, J. Worbs, H. Siekmann, J. Kirchhoff, A. Gordijn, and J. Hüpkes, *Thin Solid Films* 520, 4208 **(2012)**.
5. O. Kluth, G. Schöpe, J. Hüpkes, C. Agashe, J. Müller, and B. Rech, *Thin Solid Films* 442, 80 **(2003)**.
6. M. Boccard, C. Battaglia, S. Hänni, K. Söderström, J. Escarré, S. Nicolay, F. Meillaud, M. Despeisse, and C. Ballif, *Nano Lett.* 12, 1344 **(2012)**.

7. A. Hongsingthong, T. Krajangsang, I. A. Yunaz, S. Miyajima, and M. Konagai, *Applied Physics Express* 3, 051102 (**2010**).
8. T. Soderstrom, P. Cuony, C. Battaglia, S. Hanni, S. Nicolay, and C. Ballif, *IEEE J. Photovoltaics* 2, 229 (**2012**).
9. O. Isabella, J. Krˇc, and M. Zeman, *Appl. Phys. Lett.* 97, 101106 (**2010**).
10. G. A. C. M. Spierings, *J. Mater. Sci.* 28, 6261 (**1993**).
11. S. Kim, J.-W. Chung, H. Lee, J. Park, Y. Heo, and H.-M. Lee, *Sol. Energy Mater. Sol. Cells* 119, 26 (**2013**).
12. Y. Gotoh, A. Adachi, and M. Mizuhashi, *Reports Res. Lab. Asahi Glass Co., Ltd.* 37, 13 (**1987**).
13. Y. Chung, S. Lee, S. Bae, H. Park, J. Jung, and N. Hwang, *J. Nanosci. Nanotechnol.* 12, 5947 (**2012**).
14. Y. Wang, X. Zhang, L. Bai, Q. Huang, C. Wei, and Y. Zhao, *Appl. Phys. Lett.* 100, 263508 (**2012**).

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