

Modulation of Field Emission Properties of ZnO Nanorods During Arc Discharge

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Zinc oxide (ZnO) nanorods have been synthesized via the arc discharge method. Different oxygen partial pressures were applied in the arc discharge chamber to modulate the field emission properties of the as-synthesized ZnO nanorods. Scanning electron microscopy (SEM) was carried out to analyze the morphology of the ZnO nanorods. The ion beam analysis technique of proton induced X-ray emission (PIXE) was performed to probe the impurities in ZnO nanorods. SEM images clearly revealed the formation of randomly oriented ZnO nanorods with diameters between 10–50 nm. It was found that the morphology and the electrical properties of the ZnO nanorods were dependent on the oxygen partial pressure during arc discharge. In addition enhanced UV-sensitive photoconductivity was found for ZnO nanorods synthesized at high oxygen partial pressure during arc discharge. The field emission properties of the nanorods were studied. The turn-on field, which is defined at a current density of $10 \mu\text{A cm}^{-2}$, was about $3 \text{ V } \mu\text{m}^{-1}$ for ZnO nanorods synthesized at 99% oxygen partial pressure during arc discharge. The turn-on field for ZnO nanorods increased with the decrease of oxygen partial pressure during arc discharge. The simplicity of the synthesis route coupled with the modulation of field emission properties due to the arc discharge method make the ZnO nanorods a promising candidate for a low cost and compact cold cathode material.

Keywords: Zinc Oxide Nanorods, Arc Discharge, Field Emission.

1. INTRODUCTION

As an important wide band gap ($E_g = 3.37 \text{ eV}$) semiconductor, ZnO has received widespread attention in optical and electronic industries, because of its distinctive electrical, optoelectronic and piezoelectric properties.¹ In recent years, one-dimensional (1D) ZnO nanostructures have been studied because of their great potential for advanced optoelectronic, gas sensing and spintronics applications. Good thermal stability, oxidation resistance and a large tendency to form stable nanostructures make the ZnO nanostructures also a popular material for field emission (FE) studies.^{1–3} As is well-known, different morphologies can have a large effect on the properties of nanostructures themselves. FE has been observed from various ZnO nanostructures, including nanowires,^{4–6} nanorods,⁷ nanofibers,⁸ and chessman-like nanostructures.⁹

Up to now, various fabrication techniques have been established for the growth of ZnO nanorods, such as vapor phase transport,¹⁰ metal organic vapor phase epitaxy,¹¹ vapor liquid solid growth¹² and pulsed laser deposition.¹³ These growth methods require relatively high temperature during the synthesis procedure. Recently, low-temperature

approaches like sol-gel techniques,¹⁴ chemical vapor deposition¹⁵ and electrodeposition^{16,17} have been developed. However, these methods lack suitability for mass fabrication or inevitably introduce unwanted impurities. The arc discharge method is simple, cost-effective, rapid, and could easily be implemented and adapted for mass production. Wu et al. first reported fabrication of ZnO nanorods by arc discharge in 2006.¹⁸ Further, they obtained ZnO nanorods with small diameters by arc discharge and discussed the growth mechanism and photoluminescence properties.¹⁹ Recently, we reported the UV and humidity sensing properties of ZnO nanorods synthesized by the arc discharge method.²⁰

In this work, we report on the synthesis of ZnO nanorods with different oxygen partial pressure during arc discharge, without a catalyst. Scanning electron microscopy (SEM) was employed to study the morphology and structure of the as-synthesized ZnO nanorods. The ion beam analysis technique of proton induced X-ray emission (PIXE)²¹ was carried out to probe the impurities in the ZnO nanorods. The electrical properties of ZnO nanorods synthesized at different oxygen partial pressure during arc discharge were examined. The results highlight the opportunities for field emission applications of ZnO nanorods obtained and modulated by a simple method.

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2. EXPERIMENTAL DETAILS

A custom built arc discharge apparatus²² was used to synthesize ZnO nanorods. A zinc rod (97% purity) served as the anode and a water-cooled graphite disc as the cathode inside the process chamber. The position of the anode was adjusted by a stepper motor to move up and down to facilitate an arc discharge with a steady current.

To investigate the gas partial pressure effects on the ZnO nanorods by arc discharge, different ambient gas environments were introduced into the GNS arc discharge chamber. The total pressure was maintained at 500 Torr. A gas mixture with different oxygen ratio (a. 25% O₂ + 75% Ar, b. 50% O₂ + 50% Ar, c. 99% O₂) was introduced into the arc discharge chamber, respectively. After discharging for 20 seconds at 50 A, a bulk quantity of white materials was observed adhering to the surface of the graphite substrate and inner wall of the chamber. The as-synthesized ZnO nanorods were collected from the arc discharge chamber and SEM was performed to characterize the morphology and structure of the products.

Prototype sensors were constructed with ZnO nanorods synthesized at different oxygen partial pressures during arc discharge. Detailed information about sensor fabrication can be found in Ref. [20]. The current–voltage (*I*–*V*) characteristics of the ZnO nanorods synthesized at different oxygen partial pressures were determined by measuring

the corresponding current from the ZnO nanorods sensor with UV illumination at a wavelength of 340 nm.

To investigate the field emission property of the as-synthesized materials, the ZnO nanorods were mounted onto a metallic substrate using silver conductive paste and electrically connected to a stainless steel block. The assembly was placed in a vacuum chamber evacuated to a residual gas pressure of 2×10^{-7} mbar. The ZnO nanorods were the cathode and a highly polished stainless steel rod with a circular flat tip of 4 mm diameter served as the anode. The anode was mounted on a micro-adjustment system (μ m resolution) to set the anode–cathode separation. FE measurements were performed by applying different voltages across the stainless steel anode and the cathode in the vacuum chamber. A DC voltage was applied, and current was measured between the cathode and anode using a Keithley 237 source measure unit (Keithley Instruments Ltd., Reading, UK). The emission current was measured as a function of anode–cathode separation between 50 and 120 μ m.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM images of ZnO nanorods synthesized by arc discharge at different oxygen partial pressure of 99% (Figs. 1(a and b)), 50% (Fig. 1(c)), and 25% (Fig. 1(d)). From the image it can be seen that large

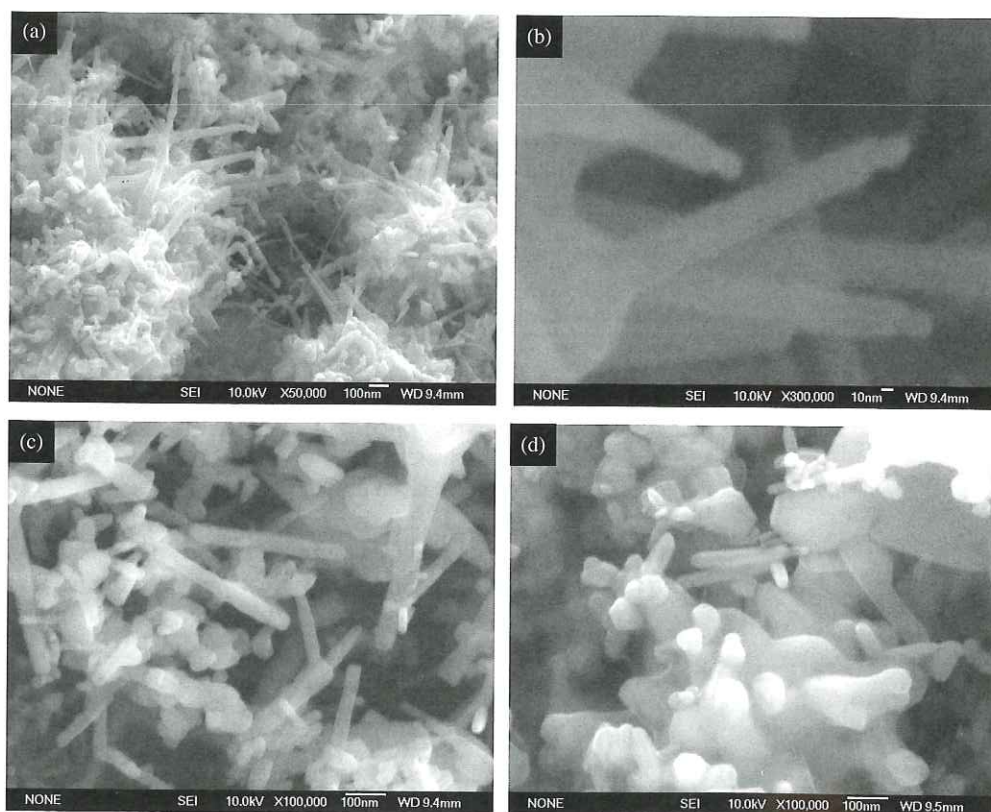


Fig. 1. SEM images of ZnO nanorods synthesized at different oxygen partial pressures during arc discharge. (a) 99% O₂, (b) 99% O₂ in high magnification, (c) 50% O₂, (d) 25% O₂.

quantity of rod shaped ZnO nanostructures were fabricated after arc discharge, which agrees well with the results reported in Ref. [19]. The diameters of the ZnO nanorods are constantly in the range of 10–50 nm, with the change of oxygen partial pressure during arc discharge. Interestingly, it was found that the morphology, especially the top and the length, of the synthesized ZnO nanorods was dependent on the oxygen partial pressure. When the oxygen partial pressure was as high as 99%, the ZnO nanorods showed a tapered shape on top and the length was in the range of 0.2–1 μm . With the decrease of the oxygen partial pressure during arc discharge, the top morphology of the ZnO nanorods became blunt and the length was reduced. The magnified SEM image shown in Figure 1(b) clearly indicates that the top of the ZnO nanorods has smaller size than for the base. While in Figures 1(c) and (d) both top and base of the ZnO nanorods have similar size. The length of the ZnO nanorods decreased from the range of 0.03–0.6 μm at oxygen partial pressure of 50% to the range of 0.02–0.2 μm at pressure of 25%. Therefore, higher oxygen partial pressure during arc discharge contributes to higher aspect ratio of the ZnO nanorods.

The as-grown ZnO nanorod powder samples were prepared as a pellet for PIXE analysis to probe the impurity in ZnO nanorods. The PIXE measurement²¹ was performed by using a 2-MeV Helium beam with the results shown in Figure 2. It is evident that only Zn $K\alpha$ and Zn $K\beta$ peaks were detected from the ZnO nanorod powder samples, which verified that the as-grown ZnO nanorods from arc discharge have very high purity.

Figure 3 shows the I - V curves for ZnO nanorods sensors with nanorods synthesized under different oxygen partial pressures during arc discharge. It can be seen that the measured current increased with the increase of the applied voltage. A photocurrent increase by nearly two orders of magnitude from 5.53×10^{-9} to 2.65×10^{-7} A was obtained for the ZnO nanorods synthesized at 99% O_2

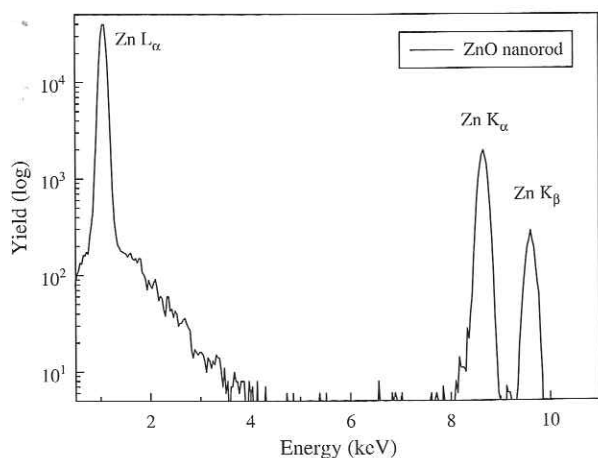


Fig. 2. PIXE spectra of ZnO nanorods powder.

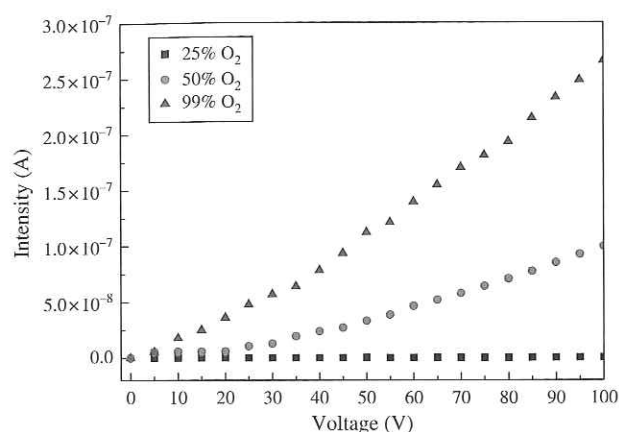


Fig. 3. I - V characteristics for ZnO nanorods sensors under UV illumination, with nanorods synthesized at different oxygen partial pressures during arc discharge. (No polymeric film-forming agent was added and the measurement was carried out under an illumination wavelength of 340 nm.)

when the bias was set as 100 V. Only one order of magnitude current increase was measured for the ZnO nanorods synthesized at 50% O_2 at the same bias. It can be seen from Figure 3 that the ZnO nanorods synthesized at 99% oxygen partial pressure exhibited the highest photocurrent under UV illumination at 340 nm when compared to ZnO nanorods synthesized at other oxygen partial pressures. The results indicate a better UV-sensitive photoconduction for ZnO nanorods synthesized at higher oxygen partial pressure during arc discharge, which is considered to be due to the special morphology of the high aspect ratio of ZnO nanorods.

As is well-known, different morphologies can have a large effect on the properties of nanostructures themselves. Both the tapered top shape and long length of the ZnO nanorods synthesized at 99% oxygen partial pressure result in a much higher aspect ratio than for the ZnO nanorods with blunt top and short length. According to the generally accepted trapping mechanism for ZnO nanostructure photosensors, more electrons will be captured near the ZnO nanorods surface with high-aspect-ratio under UV illumination. Therefore, at the same time the photoconductivity will be increased.

The growth mechanism of ZnO nanorods has been intensively investigated based on vapor-liquid-solid (VLS) processes with a catalyst or vapor-solid (VS) process without catalyst. Because no catalysts were used in our experiment, it is proposed that the ZnO nanorods growth is determined by the VS process.¹⁹ During the arc discharge, solid Zn evaporates into Zn vapors rapidly because of the high temperature at the arc center. The vaporized Zn atoms deposit onto the inner wall of the arc discharge chamber and are further oxidized into ZnO nucleuses. Subsequently those nucleuses will grow into ZnO nanorods along the [0001] direction by absorbing incoming Zn and O atoms.

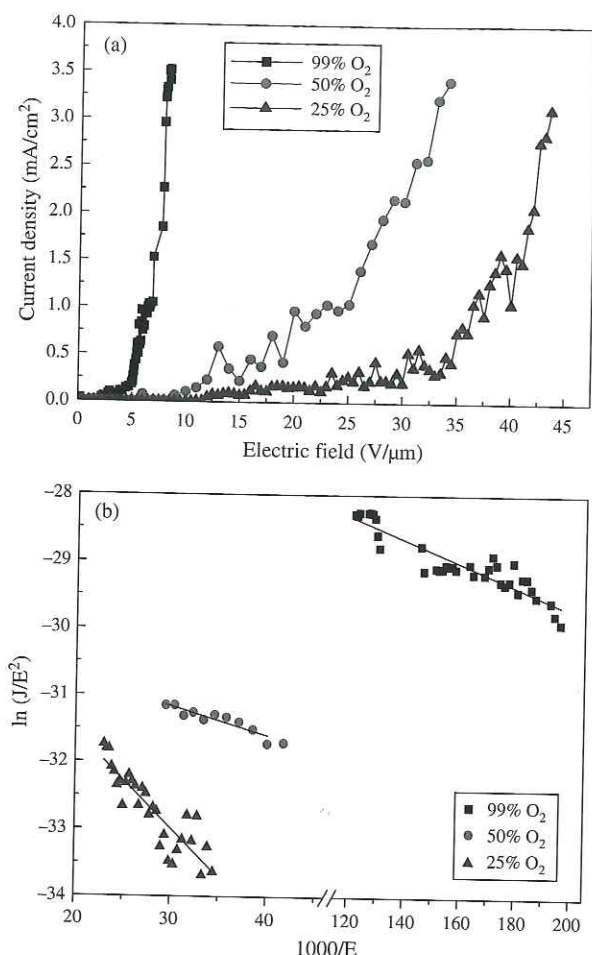


Fig. 4. (a) Field emission plot for ZnO nanorods produced using three different gas mixtures. (b) Fowler-Nordheim plots.

When the partial pressure of the oxygen is low, as the growth proceeded, less O₂ is fed into the system during arc discharge. The oxygen will be consumed rapidly in the arc discharge chamber after which the growth of ZnO nanorods will cease. Consequently, the length of the ZnO nanorods will be short, as shown in Figure 1(d). At high oxygen partial pressure, take 99% for example, both the oxygen and zinc proportion in the vapour were high enough for the growth of ZnO nanorods. That leads to longer lengths of the ZnO nanorods, as shown in Figure 1(a). Therefore, O₂ partial pressure plays an important role in the process of ZnO nanorod morphology.

The FE properties of ZnO nanorods synthesized at different oxygen partial pressures during arc discharge were investigated. Figure 4(a) shows the FE current density as a function of the applied electric field for ZnO nanorods. The ZnO nanorods synthesized at 99% O₂ partial pressure showed a turn-on electric field of 3 V μm⁻¹ at a current density of 10 μA cm⁻² and an emission current density of 1 mA cm⁻² under the threshold field of 6.6 V μm⁻¹.

To further investigate the FE property of as-grown ZnO nanorods, the Fowler-Nordheim (F-N) law⁴ was employed

to describe the exponential dependence between the emission current and the applied field.

$$J = \frac{A\beta^2 E^2}{\phi} \exp\left(-\frac{B\phi^{3/2}}{\beta E}\right)$$

where, J is the emission current density (A cm⁻²); E is the macroscopic electric field (V m⁻¹) at the emission sites, $E = V/d$, where d is the separation between the anode and the cathode and V is the applied voltage. The two constants are $A = 1.54 \times 10^{-6}$ AeV⁻² and $B = 6.83 \times 10^9$ eV^{-3/2} Vm⁻¹; ϕ is the work function of the emitter (eV) and β is the field enhancement factor introduced by the non-planar cathode surface of the nanostructures. The F-N emission behavior can be examined from the linearity of curves plotting $\ln(J/E^2)$ versus $1/E$. The enhancement factor β can be determined from the gradient of the plots and by taking a reasonable ϕ value. Figure 4(b) shows approximate linear relations between $\ln(J/E^2)$ and $1/E$ suggesting that the electron emission could be well formulated by the F-N theory for the ZnO nanorods. Using 5.3 eV as the work function for ZnO, we obtained values of the enhancement factor of ZnO nanorods synthesized at different oxygen partial pressures during arc discharge, as listed in Table I. It is obvious that the ZnO nanorods synthesized at 99% O₂ have lower turn-on field and threshold field than those synthesized at 50% and 25% O₂ partial pressure.

With the same work function, the field enhancement factor of the emitters is the key feature for FE properties. Generally, it is well agreed that FE properties mainly depend on the top morphology and the density of one-dimensional nanostructures. The emitter which has a sharper top has better FE properties. Since the ZnO nanorods synthesized at 99% oxygen partial pressure have sharper tops compared with those nanorods synthesized at low oxygen partial pressure during arc discharge, it is reasonable that electrons can be more easily emitted from ZnO nanorods with a sharper top than from a blunt top. The low turn-on field and threshold field for the ZnO nanorods synthesized at 99% oxygen partial pressure may result from the tapered shape of top.

Therefore, the field enhancement factor β can be modulated with the change of oxygen partial pressure during arc discharge, which will play a key role in modulating the FE characteristics of ZnO nanorods. It is demonstrated that the arc discharge method is not only a promising way

Table I. Turn-on field, threshold field and field enhancement factor of the ZnO nanorods synthesized at different oxygen partial pressures during arc discharge.

ZnO nanorods synthesized at different oxygen ratio	Turn-on field (V μm ⁻¹)	Threshold field (V μm ⁻¹)	Field enhancement factor (β)
99%	3	6.6	4790
50%	7.8	22.1	1940
25%	11.5	36.5	580

to mass produce ZnO nanorods but also an easy way to modulate both the photoconductivity and the FE properties of ZnO nanorods.

4. CONCLUSIONS

ZnO nanorods have been synthesized via the arc discharge method. SEM analysis clearly revealed the formation of randomly oriented ZnO nanorods with diameters between 10–50 nm. The ZnO nanorods have been analysed by the PIXE, revealing high purity material. Different oxygen partial pressures were applied in arc discharge chamber to modulate the electrical properties of the ZnO nanorods. It was found that the morphology and the aspect ratio of the synthesized ZnO nanorods were dependent on the oxygen partial pressure. An enhanced UV-sensitive photoconductivity was found for ZnO nanorods synthesized at higher oxygen partial pressure during arc discharge. Field emission has been measured from the nanorods. The ZnO nanorods synthesized at 99% oxygen partial pressure during arc discharge shown a turn-on field of 3 V/ μm at a current density of 10 $\mu\text{A}/\text{cm}^2$ and an emission current density of 1 mA cm^{-2} under the threshold field of 6.6 V μm^{-1} . The field enhancement factor β of the ZnO nanorods can be modulated with the change in oxygen partial pressure during arc discharge, indicating that the field emission of ZnO nanorods can be controlled by adjusting the oxygen partial pressure during the arc discharge.

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References and Notes

1. C. J. Park, D. K. Choi, J. Yoo, G. C. Yi, and C. J. Lee, *Appl. Phys. Lett.* 90, 083107 (2007).
2. Q. Wang, K. Yu, T. H. Wang, and C. L. Lin, *Appl. Phys. Lett.* 83, 2253 (2003).
3. H. Jin, Y. Li, J. Li, and C. Gu, *Microelectron. Eng.* 86, 1159 (2009).
4. C. J. Lee, T. J. Lee, S. Lyu, C. Lyu, and Y. Zhang, *Appl. Phys. Lett.* 81, 3648 (2002).
5. K. Park, Y. Choi, M. Ahn, D. Kim, Y. Sung, J. Park, and K. Choi, *J. Nanosci. Nanotechnol.* 9, 4328 (2009).
6. K. Huo, J. Fu, H. Ni, Y. Hu, G. Qian, P. K. Chu, and Z. Hu, *J. Nanosci. Nanotechnol.* 9, 3848 (2009).
7. Q. Zhao, X. Y. Xu, X. F. Song, X. Z. Zhang, D. P. Yu, C. P. Li, and L. Guo, *Appl. Phys. Lett.* 88, 033102 (2006).
8. C. X. Xu, X. W. Sun, and B. J. Chen, *Appl. Phys. Lett.* 84, 1540 (2004).
9. J. Xiao, *Mater. Chem. Phys.* 115, 771 (2009).
10. A. Umar, Y. K. Park, and Y.-B. Hahn, *J. Nanosci. Nanotechnol.* 9, 2692 (2009).
11. B. P. Zhang, N. T. Binh, K. Wakatsuki, Y. Segawa, Y. Kashiwaba, and K. Haga, *Nanotechnology* 1, S382 (2004).
12. D. Banerjee, J. Rybczynski, J. Y. Huang, D. Z. Wang, K. Kempa, and Z. F. Ren, *Appl. Phys. A* 80, 749 (2005).
13. M. Lorenz, E. M. Kaidashev, A. Rahm, T. Nobis, J. Lenzner, G. Wagner, D. Spemann, H. Hochmuth, and M. Grundmann, *Appl. Phys. Lett.* 86, 143113 (2005).
14. Y. W. Chen and Y. C. Liu, *J. Chem. Phys.* 12, 134701 (2005).
15. J. J. Wu and S. C. Liu, *Phys. Chem. B* 106, 9546 (2002).
16. S. Peulon and D. Lincot, *Adv. Mater.* 8, 166 (1996).
17. S. Chatterjee, S. Gohil, B. Chalke, and P. Ayyub, *J. Nanosci. Nanotechnol.* 9, 4792 (2009).
18. X. F. Wu, C. X. Xu, G. P. Zhu, and Y. M. Ling, *Chin. Phys. Lett.* 23, 2165 (2006).
19. G. P. Zhu, C. X. Xu, X. F. Wu, Y. Yang, X. W. Sun, and Y. P. Cui, *J. Electronic Materials* 36, 494 (2007).
20. F. Fang, J. Futter, A. Markwitz, and J. Kennedy, *Nanotechnology* 20, 245502 (2009).
21. J. Kennedy, A. Markwitz, B. J. Ruck, S. M. Durbin, and W. Gao, *J. Electronic Materials* 36, 472 (2007).
22. J. Kennedy, J. Futter, F. Fang, and A. Markwitz, *New Zealand Patent Application* 576207 (2008).

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