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J. Mater. Sci. Technol., 2013, 29(10), 893−897

JMST

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Rapid Synthesis of Piezoelectric ZnO-Nanostructures for Micro Power-Generators

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[Manuscript received January 3, 2013, in revised form April 4, 2013, Available online 18 July 2013]

In this paper, we report a rapid synthesis of piezoelectric ZnO-nanostructures and fabrication of the nanostructures-based power-generators demonstrating an energy conversion from an environmental mechanical/ultrasonic energy to an electrical energy. The ZnO nanostructures are grown on a silicon wafer by a modified chemical solution method (CSD, chemical-solution-deposition) with a two-step thermal-oxidation approach. The synthesis process can be completed within 1 h. By varying the mixture-ratio of Zn micro-particles in an oxalic acid solution with 0.75 mol/l concentration in the CSD process, the growth mechanism is well-controlled to synthesize three different types of ZnO-nanostructures (i.e., dandelion-like nanostructures, columnar nanostructures, and nanowires). Furthermore, through oxidizing at different temperatures in the thermal-oxidation process, the featured geometry of the nanostructures (e.g., the length and diameter of a nanowire) is modified. The geometry, size, morphology, crystallization, and material phase of the modified nanostructures are characterized by scanning electron microscopy and X-ray diffraction. Finally, the nanostructures are used to fabricate several micro power-generators. Through the piezoelectric effect, a maximum current density output of 0.28 μA cm^{-2} generated by a power-generator under an ultrasonic wave is observed.

KEY WORDS: Piezoelectric ZnO nanostructures; Chemical solution method; Thermal-oxidation; Power-generator

1. Introduction

Zinc oxide (ZnO), a semiconducting material owing a wide bandgap up to 3.37 eV with a large excitation binding energy up to 60 meV[1], has attracted considerable interests due to its diverse applications in the multi-discipline field of the engineering, material science, and biomedical technology. Furthermore, due to the novel functionalities exhibiting in nanostructured materials, several excellent optoelectronic properties such as the transparent-conducting characteristics have been demonstrated by the nanostructured ZnO materials. Thus, the ZnO nanostructures are the perfect candidate for applications in nanoscale ultraviolet lasers, light-emitting diodes, photodetectors, and chemical sensors[2−5]. Recently, the piezoelectric property of the ZnO nanostructures has received lots of attentions in the application of energy-harvesting[6−11]. To grow ZnO nanostructures exhibiting a decent piezoelectric property for energy-harvesting application, various synthesis approaches have been developed such as metallorganic chemical-vapor-deposition[12], vapor-phase transportation[13], sputtering[14], sol−gel[15], thermal evaporation[16], and vapor−liquid−solid[17,18]. Due to the featured characteristics of the synthesis approaches, specific ZnO nanostructures including nanocombs, nanotubes, nanowires, nanorods, and nanoflowers[19−23] have been synthesized in order to demonstrate featured piezoelectric properties for energy-harvesting. However, in practical, these approaches have drawbacks such as complicated, expensive, and/or low throughput rate for mass production of the ZnO nanostructures. Therefore, a simple and cheap synthesis with a high throughput rate is needed. Hence, in this paper, we provide a modified chemical-solution-deposition (CSD) with a two-step thermal-oxidation approach to simplify the synthesis process with increasing the throughput rate capable of massively producing the featured ZnO nanostructures. Furthermore, several piezoelectric power-generators consisting of the ZnO nanostructures are tested under an ultrasonic wave in order to investigate the piezoelectric property of the ZnO nanostructures.

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http://dx.doi.org/10.1016/j.jmst.2013.07.005

2. Experimental

2.1. Synthesis and characterization of ZnO nanostructures

Through utilizing our approach, the growth mechanism of the ZnO-nanostructures is described below. In the thermal-oxidation process of the metallic Zn powders, the $ZnC_2O_4 \cdot H_2O$ layer is formed on the surface of the Zn powders while oxidized below 190 °C in oxygen. When the powders are heated to the melting temperature of oxalic acid at 190 °C in air[24], the $ZnC_2O_4 \cdot H_2O$ compound layer is gradually transformed into a layer of ZnO. The corresponding chemical reaction is expressed below:

$$2Zn + O_2 + 2H_2C_2O_4 \rightarrow 2ZnC_2O_4 + 2H_2O \quad (1)$$

$$ZnC_2O_4 \rightarrow ZnO + CO + CO_2 \quad (2)$$

However, the oxide layer is unstable when the oxygen atoms tend to diffuse out of the oxide layer at high temperatures[25,26]. Therefore, the Zn atoms are able to interact with the diffusing oxygen atoms to form ZnO nanostructures.

According to the growth mechanism of the ZnO-nanostructures, the corresponding synthesis process is set as follows. Zinc metal powder of 1 g (purity: 99.9%) was mixed with an oxalic acid solution (concentration: 0.75 mol/l) of different volume ranging from 10 to 200 ml. The diameter of the powder is approximate 500 nm. The mixed solutions were stirred in an ultrasonic-shaker for 10 min and subsequently deposited on Si wafers through a dropper. After this, the Si wafers (with the mixed solutions on the top of the wafers) were heated and oxidized at 190 °C in air for 1 min to transform the solutions into thin films. The films on the top of the wafers are used as the substrates. In the synthesis procedure, the substrates were placed inside a quartz tube of a single-tube furnace (Olink, OT-060-30). The quartz tube was vacuumed while the temperature was raised at a constant ramping rate of 20 °C/min. Subsequently, the substrates were heated at different temperatures ranging from 350 to 700 °C for 20 min. After heating, the substrates were cooled down to room temperature. The geometry, size, morphology, crystallization, and material phase of the synthesized ZnO nanostructures were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2.2. Fabrication and testing of ZnO-nanostructures-based micro power-generators

After the ZnO-nanostructures were synthesized, several power-generators consisting of the ZnO-nanostructures were fabricated to investigate the piezoelectric response influenced by the nanostructures. Fig. 1 is an illustration of the micro power-generators consisting of the ZnO nanostructures we synthesized. The top substrate was fabricated by growing α-Fe_2O_3 nanowires on a flexible FeNi (1:1) alloy sheet with a thickness of 0.1 mm prepared through a vapor−solid process. That is, the FeNi sheet was ultrasonically cleaned in ethanol for 10 min and subsequently heated to 600 °C at a constant ramping rate of 20 °C/min with oxygen in a quartz tube in a furnace. The quartz tube was vacuumed and consequently Ar flowed into the tube at a flux rate of 50 sccm (standard-state cubic centimeter per minute) for 20 min. After

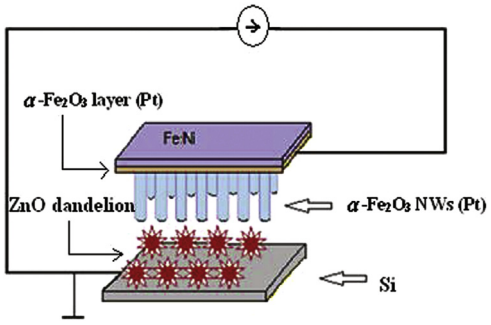

Fig. 1 An illustration of a piezoelectric power-generator consisting of dandelion-like nanostructures demonstrating an energy conversion from mechanical/ultrasonic energy to electrical energy.

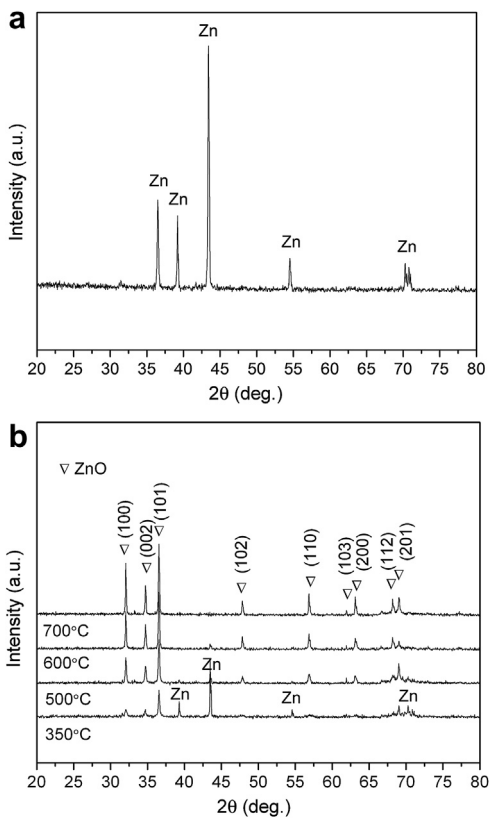

Fig. 2 XRD patterns of metallic Zn powders (a) and synthesized products (b) on a silicon wafer by using the oxalic acid solution of 10 ml at different oxidizing temperatures ranging from 350 to 700 °C for 20 min.

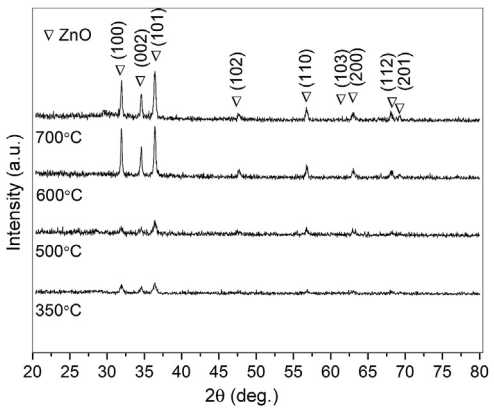

Fig. 3 XRD patterns of synthesized products on a silicon wafer by using the oxalic acid solution of 60 ml at different oxidizing temperatures ranging from 350 to 700 °C for 20 min.

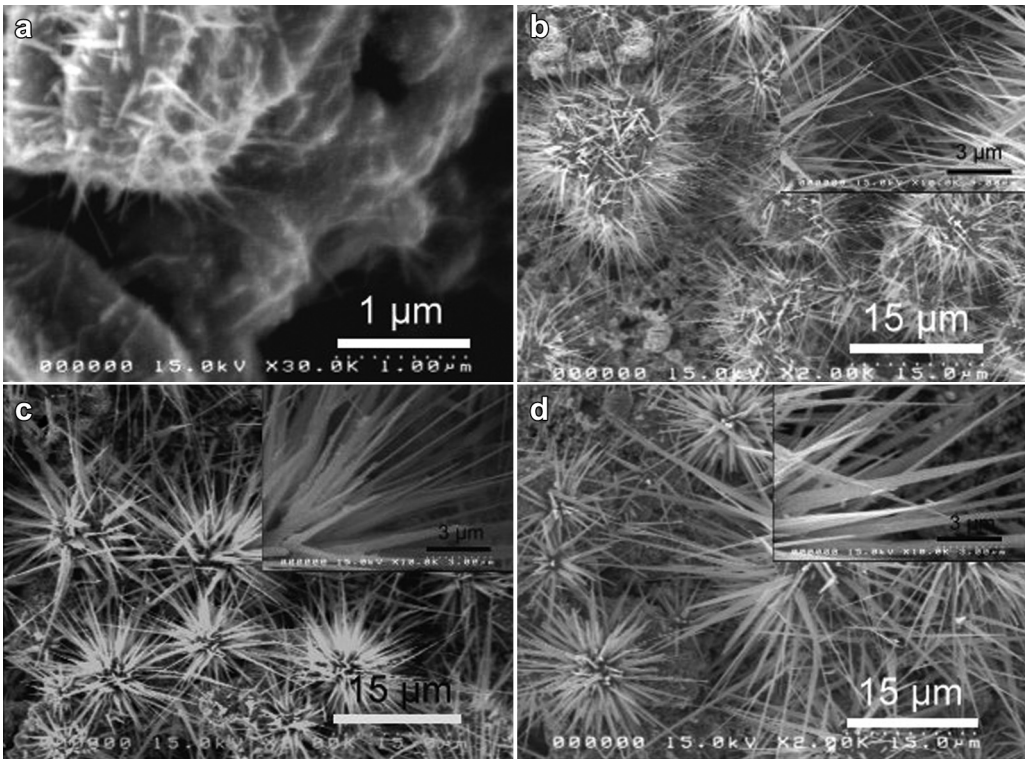

Fig. 4 SEM images of ZnO nanostructures synthesized by using the oxalic acid solution of 10 ml at the oxidizing temperatures of 350 °C (a), 500 °C (b), 600 °C (c), and 700 °C (d) for 20 min.

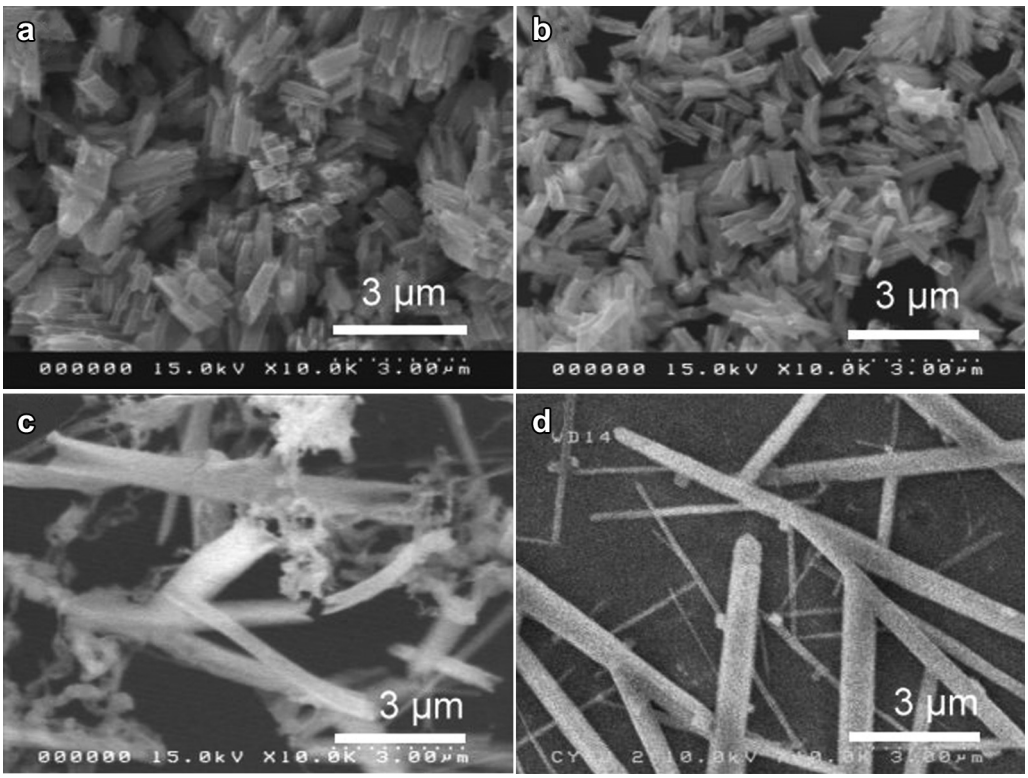

Fig. 5 SEM images of ZnO nanowires synthesized by using the oxalic acid solution of 60 ml (a), 100 ml (b), 150 ml (c), and 200 ml (d) at the oxidizing temperature of 700 °C.

cooling to room temperature, α-Fe_2O_3 nanowires were formed on the substrate[27]. After this, a platinum thin-film with a thickness of 10 nm was deposited on the α-Fe_2O_3-NWs/FeNi-sheet using an auto-fine coater (JFC-1600) in order to create a Schottky contact between the top substrate and ZnO-nanostructures/substrate[28]. The two substrates were fixed along the edge of the substrates by adhesive binding as the power-generators. The current−voltage characteristics of the power-generators were measured by using a

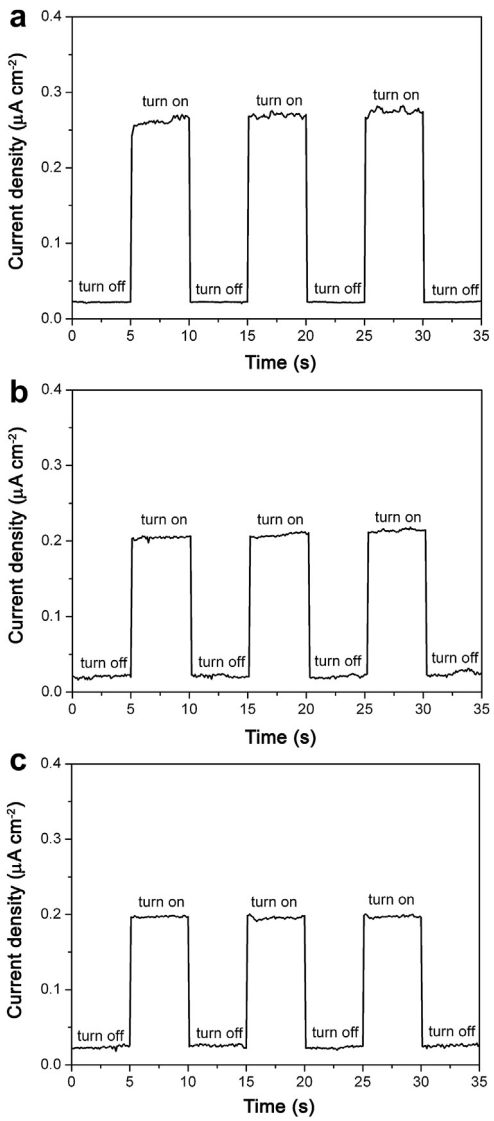

Fig. 6 Under an ultrasonic-wave vibration at 46 kHz for 5 s, the piezoelectric current response of the power-generator consisting of ZnO nanostructures synthesized by using the oxalic acid solution of 10 ml (a), 60 ml (b), and 200 ml (c) with a concentration of 0.75 mol/l at the oxidizing temperature of 700 °C for 20 min.

digital multimeter (Agilent 34970A). The micro-current generated by the power-generators (i.e., the piezoelectric response of the power-generators) was tested by driving ultrasonic waves (Evergreen Ultrasonic Group, EGC-50) with a frequency of 46 kHz through the ZnO nanostructures.

3. Results and Discussion

As shown in Fig. 2(a), the Zn powders crystallized in nature show distinguished peaks at 36.5°, 39.2°, 43.4°, 54.5°, 70.3°, and 70.9° in XRD patterns. After the substrate is thermally oxidized in vacuum for 20 min, new peaks at 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, 62.9°, 66.4°, 67.9° and 69.1° of the ZnO are produced. Fig. 2(b) shows the XRD patterns of the substrates prepared with 10 ml oxalic acid solution at oxidizing temperatures ranging from 350 to 700 °C in vacuum. Fig. 2(a) indicates that the intensity of Zn is gradually decreased while the oxidizing temperature is increased. The peaks of Zn entirely vanished when the substrate was heated to 700 °C. This shows that the peaks of the ZnO crystal completely substitute those of Zn in the XRD pattern. Moreover, the ZnO crystalline exhibits a wurtzite-structure, which is consistent with the standard ZnO bulk crystal (JCPDS No. 36-1451)[29].

Fig. 3 shows the XRD patterns of ZnO-nanostructures grown on the substrates by using the oxalic acid solution of 60 ml in the two-step thermal-oxidation process. In Fig. 3, the XRD patterns show that the peaks of Zn are entirely substituted by those of ZnO crystalline when the oxidizing temperature is higher than 350 °C[24]. This is caused by more zinc atoms reacting with the oxalic acid solution in the CSD process to transform into zinc oxalate when the volume of oxalic acid solution used is increased. Due to this, the ZnO crystalline is easier to be synthesized even at low temperature.

Fig. 4 shows SEM images of ZnO-nanostructures grown on Si substrates by the two-step thermal-oxidation method with 10 ml oxalic acid solution. Fig. 4(a−d) shows the grown nanostructure is dandelion-like. In addition, the diameter and length of the nano-fiber in the dandelion-like nanostructure are increased while the operating temperature is increased. The insets of Fig. 4(b−d) are the corresponding magnified SEM images. As shown in the magnified SEM images, the average length and diameter of the nanostructures increases from 0.5 μm to 15 μm and 30 nm to 400 nm, respectively, while the operating temperature is increased from 350 to 700 °C.

Fig. 5 shows the transformed nanostructures grown by the two-step thermal-oxidation process at the oxidizing temperature of 700 °C when the volume of the oxalic acid solution is changed. Fig. 5(a−d) shows SEM image of the ZnO products synthesized by using the oxalic acid solution of 60, 100, 150 and 200 ml, respectively. The synthesized nanostructures are transformed from a dandelion-like nanostructure to a cluster of nanorods by adding the oxalic acid solution to 60 ml. Furthermore, the nanorods are transformed to separated nanowires when the oxalic acid solution is added to 200 ml. These experimental results show that the synthesized nanostructure transforms from dandelion-like nanostructures to nanorods, and to nanowires when the volume of the oxalic acid solution is increased from

Table 1 Piezoelectric current response of the power-generators consisting of various ZnO nanostructures

ZnO-nanostructure	Synthesis/growth method of the nanostructures	Synthesis/growth time (h)	Output current density (nA cm^{-2})	Ref.
Nanowires	VLS (with catalyst)	4	60	[8]
	Wet-chemical method	39	50	[9]
	Two-step thermal-oxidation	1	200	This work
Nanorods	VLS (with catalyst and gases)	−	24	[10]
	Wet-chemical method	4	90 (without bending) 300−1200 (bending)	[11]
	Two-step thermal-oxidation	1	220	This work
Nanodandelions	Two-step thermal-oxidation	1	280	This work

10 ml to 60 ml and to 200 ml in the synthesis process. Moreover, the average length and diameter of the synthesized ZnO nanostructures are increased when the oxidizing temperature in the thermal-oxidation approach is increased.

When an ultrasonic vibration at 46 kHz is applied to a power-generator for 5 s, the corresponding current response due to the piezoelectric effect is shown in Fig. 6. Fig. 6(a−c) indicates that the piezoelectric current density output decreases from 0.28 μA cm^{-2} to 0.22 μA cm^{-2} and to 0.2 μA cm^{-2} when the volume of the mixed oxalic acid solution increases from 10 ml to 60 ml and to 200 ml. The current disappears when the ultrasonic wave is removal. Due to these, it can be concluded that the power-generator consisting of dandelion-like ZnO nanostructures with α-Fe_2O_3 nanowires has a large effective contact-area under the ultrasonic-wave vibration applied to the power-generator. This results in producing the maximum piezoelectric current response (i.e., the highest current output). Finally, the obtained experimental result of the power-generator is compared with the results of other representative power-generators using ZnO nanostructures. The comparison of results is shown in Table 1. According to the comparison, the synthesis process of the ZnO nanostructures of our power-generators is more simple and rapid than the other fabrication/synthesis/growth processes of ZnO nanostructures of other power-generators. Under the ultrasonic-wave vibration, the power-generator consisting of the dandelion-like ZnO nanostructures is capable of producing a higher piezoelectric current output than the other power-generators consisting of ZnO nanostructures. However, the piezoelectric current output generated by the power-generator consisting of the dandelion-like ZnO nanostructures is less than the power-generators consisting of the ZnO nanorods grown on a flexible substrate of the generator, when a bending is applied to the generators (that is, the flexible ZnO-nanostructure-based power-generators are capable of experiencing a larger strain resulting in producing a higher piezoelectric current output[7,11]). However, the throughput rate of massive production of the flexible ZnO-nanostructures-based power-generators is too low because the fabrication/synthesis/growth process of the ZnO-nanostructures is complicated and time-consuming. Thus, our synthesis approach is more useful in practical when being compared with other fabrication/synthesis/growth process.

4. Conclusion

ZnO-nanostructures have been successfully synthesized on a silicon wafer by a rapid modified CSD method with a two-step thermal-oxidation approach. By varying the mixture-ratio of the Zn micro-powders and oxalic acid solution in the CSD process, three different types of ZnO nanostructures (dandelion-like nanostructures, nanorods, and nanowires) were grown on the silicon wafer. In addition, raising the oxidizing temperature increases the average diameter and length of the grown nanostructures. The nanostructures were used to fabricate several micro power-generators. When an ultrasonic wave is applied to the power-generators, piezoelectric current response is produced due to the piezoelectric effect. The maximum piezoelectric current density output reaches 0.28 μA cm^{-2} in the case of using dandelion-like ZnO-nanostructure in the power-generator. In the future, the density of α-Fe_2O_3 nanowires grown on the top substrate can be significantly increased in order to enlarge the effective contact-area between the top substrate and ZnO-nanostructures/substrate. The enlarged effective contact-area will significantly increase the piezoelectric current response produced by the power-generator under an ultrasonic wave.

Acknowledgments

The authors would like to thank the National Science Council of the Republic of China, Taiwan, for financially supporting this research under Contract No. NSC 101-2218-E-539-001 and NSC 102-2623-E-539-001-ET.

REFERENCES

[1] Y. Chen, D.M. Bagnall, H. Koh, K. Park, K. Hiraga, Z. Zhu, T. Yao, J. Appl. Phys. 84 (1998) 3912−3918.
[2] P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, H. Choi, Adv. Funct. Mater. 12 (2002) 323−331.
[3] C.H. Liu, J.A. Zapien, Y. Yao, X.M. Meng, C.S. Lee, S.S. Fan, Y. Lifshitz, S.T. Lee, Adv. Mater. 15 (2003) 838−841.
[4] H. Kind, H. Yan, B. Messer, M. Law, P. Yang, Adv. Mater. 14 (2002) 158−160.
[5] Q. Wan, Q.H. Li, Y.J. Chen, T.H. Wang, X.L. He, J.P. Li, C.L. Lin, Appl. Phys. Lett. 84 (2004) 3654−3656.
[6] S. Xu, Y. Qin, C. Xu, Y. Wei, R. Yang, Z.L. Wang, Nat. Nanotech. 5 (2010) 366−373.
[7] G. Zhu, R. Yang, S. Wang, Z.L. Wang, Nano Lett. 10 (2010) 3151−3155.
[8] X. Wang, J. Song, J. Liu, Z.L. Wang, Science 316 (2007) 102−105.
[9] J. Zhang, M.K. Li, L.Y. Yu, L.L. Liu, H. Zhang, Z. Yang, Appl. Phys. A 97 (2009) 869−876.
[10] T.H. Fang, W.J. Chang, W. Water, C.C. Lee, Physica E 42 (2010) 2139−2142.
[11] W.Y. Chang, T.H. Fang, C.I. Weng, S.S. Yang, Appl. Phys. A 102 (2011) 705−711.
[12] J.Y. Park, Y.S. Yen, Y.S. Hong, H. Oh, J.J. Kim, S.S. Kim, Compos. B-Eng. 37 (2006) 408−412.
[13] X. Song, Y. Zhang, J. Zheng, X. Li, J. Phys. Chem. Solids 68 (2007) 1681−1684.
[14] K.K. Kim, J.H. Song, H.J. Jung, W.K. Choi, S.J. Park, J.H. Song, J. Appl. Phys. 87 (2000) 3573.
[15] G.Z. Jia, Y.F. Wang, J.H. Yao, J. Phys. Chem. Solids 73 (2012) 495−498.
[16] K.M.K. Srivatsa, D. Chhikara, M.S. Kumar, J. Mater. Sci. Technol. 27 (2011) 701−706.
[17] E.W. Petersen, E.M. Likovich, K.J. Russell, V. Narayanamurti, Nanotechnology 20 (2009) 405603.
[18] C.K. Xu, M. Kim, S.Y. Chung, D.E. Kim, Solid State Commun. 132 (2004) 837−840.
[19] K. Yu, Q. Zhang, J. Wu, L. Li, Y. Xu, S. Huang, Z. Zhu, Nano Res. 1 (2008) 221−228.
[20] Y. Tang, D. Zhao, J. Chen, N. Wanderka, D. Shen, F. Fang, Z. Guo, J. Zhang, X. Wang, Mater. Chem. Phys. 121 (2010) 541−548.
[21] X. Kong, X. Sun, X. Li, Y. Li, Mater. Chem. Phys. 82 (2003) 997−1001.
[22] Z. He, Q. Zhang, Y. Li, H. Wang, Mater. Chem. Phys. 119 (2010) 222−229.
[23] N. Zhang, R. Yi, R. Shi, G. Gao, G. Chen, X. Liu, Mater. Lett. 63 (2009) 496−499.
[24] N.F. Hsu, M. Chang, Mater. Chem. Phys. 135 (2012) 112−116.
[25] J. Zhang, N. Li, Oxid. Met. 63 (2005) 353−381.
[26] M. Ohring, The Materials Science of Thin Films, second ed., Academic Press, San Diego, 2002.
[27] M. Chang, N.F. Hsu, China J. Chem. Phys. 24 (2011) 109−114.
[28] Z.L. Wang, J.H. Song, Science 312 (2006) 242−246.
[29] J. Lv, W. Gong, K. Huang, J. Zhu, F. Meng, X. Song, Z. Sun, Super. Micro. 50 (2011) 98−106.