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Directed Growth and Microwave Absorption Property of Crossed ZnO Netlike Micro-/Nanostructures

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Received: January 13, 2010; Revised Manuscript Received: May 5, 2010

Three-dimensional ZnO micro/nanorod networks were synthesized through the direct evaporation of metal zinc and graphite powders in Ar and O₂ at 910 °C without any catalyst. The micro/nanorod networks of as-synthesized ZnO were characterized by using scanning electron microscopy, high-resolution transmission electron microscopy, and X-ray diffraction. The branches within one network show very regular cross orientation. The nanorods follow a growth direction [0001]. Microwave absorption properties of the ZnO netlike structures have been investigated in detail. The reflection loss (RL) of the netlike structures and nanotetrapod-shaped ZnO were calculated by using the relative complex permeability and permittivity. And the value of minimum RL for the composite with 50 vol % ZnO netlike structures is −37 dB at 6.2 GHz with a thickness of 4.0 mm. These results provide a wide insight for the netlike structure ZnO as desirable materials for the fabrication of micro/nanoscale functional electromagnetic shield devices.

1. Introduction

Wurtzite-structured ZnO is of great importance for its versatile applications in optoelectronics, photovoltaics, and sensors.¹ One-dimensional (1D) nanostructures of ZnO, such as nanowires,² nanobelts,³ and nanotetrapods,⁴ have been a hot research topic in nanotechnology for their unique properties and potential applications. Moreover, several types of three-dimensional (3D) ZnO nanostructures have been synthesized. Recently, Wang et al. reported that the crossed networks of ZnO nanorods were grown on an MgO (001) substrate by controlling the growth conditions. And the grating network nanostructure of ZnO similar to the microstructure of a butterfly wing was fabricated in air by the vapor-phase transport method, using Zn powder as the source.^{5–7} Because of the high surface/volume ratio and integrated platform, 3D oxide networks have been demonstrated for building ultrasensitive and highly selective gas sensors and optoelectronics applications.^{8,9} It is worth mentioning that the ZnO nanostructures have shown great attraction for microwave radiation absorbing and shielding material in the high-frequency range due to their many unique chemical and physical properties.^{10–13} Some research works focused on ZnO as a vivid microwave absorption material due to their high surface/volume ratio and semiconductor properties. For example, the excellent microwave absorption property of ZnO dendritic nanostructure was presented by Yan et al., and the value of minimum reflection loss (RL) is −42 dB with a thickness of 5.0 mm.¹⁰ Wang et al.¹³ revealed the microwave absorption varies from the different concentration of nanowires in composites. Among previous reports, some of the research was focused on the fabrication of 3D structures and other research has shown the great interest in excellent microwave absorption properties. However, except for nanowires and nanodendrites, the influences of other

morphologies of ZnO nanostructures on the absorption property were seldom studied.^{10,14} It is necessary to study the absorption properties of these unique nanostructures and the intrinsic origin for microwave absorption of the ZnO nanocomposites.

In our work, the unique structure of 3D ZnO micro/nanorods networks was obtained through a simple thermal evaporation process. And the microwave absorption performances of ZnO netlike microstructures/paraffin composites have been investigated in detail. For comparison, the complex permittivity (ϵ) of both 3D netlikes ZnO and nanotetrapod-shaped ZnO (T-ZnO) were tested, respectively, in order to clarify the microwave absorption mechanism.

2. Experimental Details

The ZnO netlike micro/nanostructures were fabricated by the following procedure. First, high purity Zn (99.99%) and graphite powders with a molar ratio of 10:1 were ground fully into a mixture before being loaded into a quartz boat. The Si substrate with the polished side facing the powder was fixed upon the boat, and the boat with the mixture was placed at the center of the furnace. The vertical distance between the zinc source and the substrate was about 4–6 mm. And then the alumina ceramics boat was inserted into a quartz tube (30 mm inside diameter) of a tubular furnace under a constant flow of argon and oxygen. The flow rate of argon was 100 standard cubic centimeters per minute (sccm) and the fraction of oxygen was 4 sccm. The quartz tube was heated to 910 °C, and the reaction temperature was maintained for 30 min. After the evaporation was finished, a layer of woollike product was formed on the walls of the boat and the surface of the substrate. Additionally, as for T-ZnO samples measured in microwave absorption property, they were produced by employing the direct reaction of Zn and zinc acetate (ZAc) via the thermal evaporation method in our previous work.⁴

The morphologies and structures of the synthesized product were characterized by using X-ray powder diffraction (XRD) (Rigaku DMAX-RB, Japan), scanning electron microscopy

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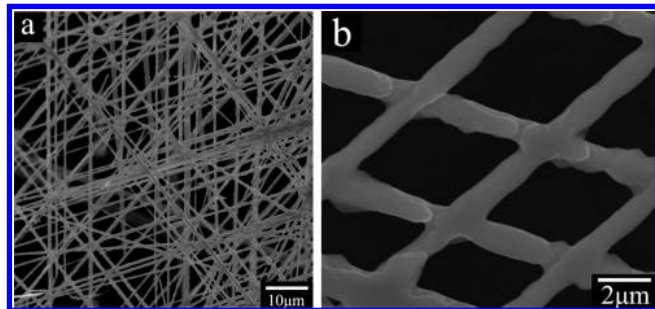


Figure 1. SEM images of ZnO netlike microstructures: (a) low magnification and (b) high magnification.

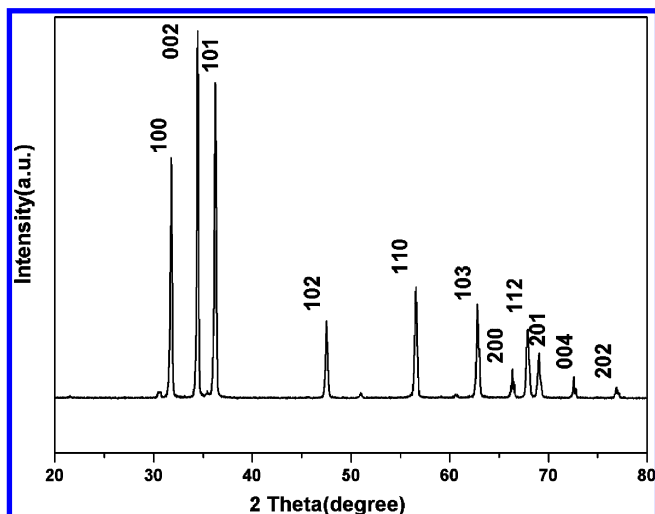


Figure 2. XRD pattern of the ZnO netlike microstructures.

(SEM) (JEOL-6490, Japan), high-resolution transmission electron microscopy (HRTEM) (JEOL-2010, Japan), and selected area electron diffraction (SAED).

Both 3D netlikes ZnO and T-ZnO composite samples used for microwave absorption measurement were prepared by mixing the ZnO netlike micro/nanostructures and the T-ZnO with paraffin wax with 50 vol % of the ZnO, respectively. The composite samples were then pressed into a compact cylindrical shape ($\varphi_{\text{out}} = 7.00$ mm; $\varphi_{\text{in}} = 3.04$ mm) for the tests of the complex permittivity ϵ and permeability μ by using a Reflectivity Scanning Measurement System HP 83751B integrated signal source and an HP 8757E vector network analyzer working at the 2–18 GHz band.

3. Results and Discussion

In our experiments, the ZnO micro/nanostructures were deposited on Si substrate without using any catalysts. During a vapor deposition process that has been widely used for growing ZnO NWs,¹⁵ when the vapor concentration was significantly increased by reducing the volume of the growth chamber, a 3D structures growth condition could be reached and ZnO netlike micro/nanostructures were formed on the (001) Si surface. The SEM images in Figure 1 show the morphologies of ZnO netlike microstructures. It can be clearly seen that these ZnO micro/nanorods formed a crossed network, and the rods have a diameter in the range of 0.2–2 μm and a length of 50–100 μm (Figure 1a). The high-magnification image of the partial network is shown in Figure 1b and the ZnO rods have a diameter of 1–2 μm . Also, Figure 1b indicates the ZnO microrods with a rough surface, possibly due to the competition between surface energy and strain energy.¹⁶ The obtained unique ZnO networks

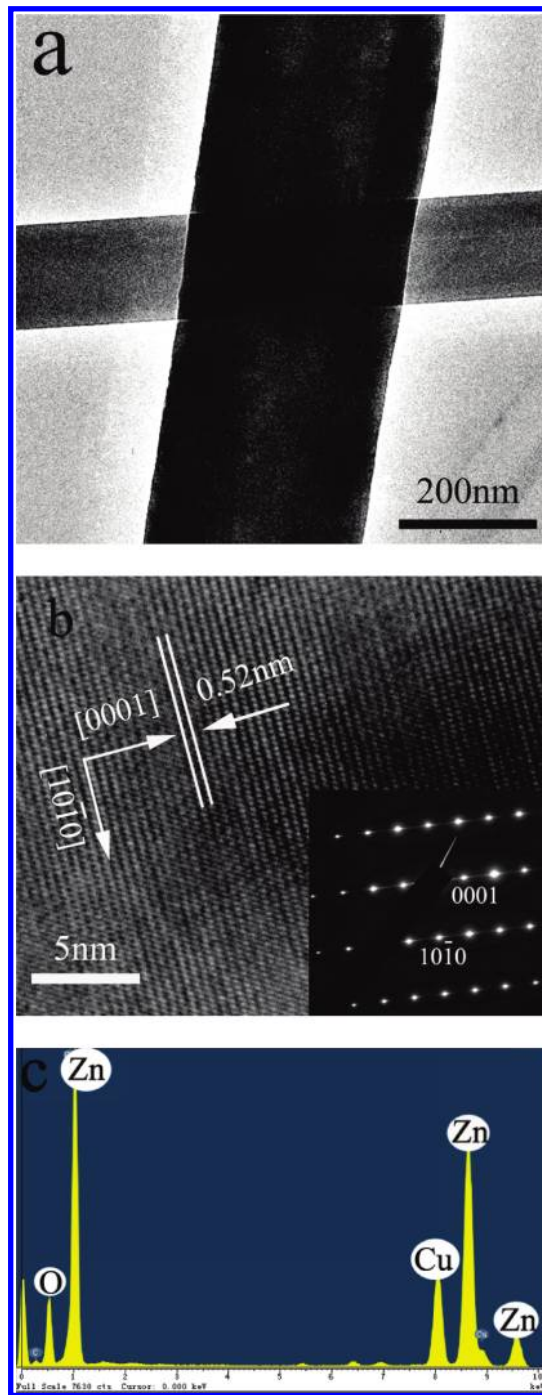


Figure 3. (a) The low-magnified TEM image of ZnO netlike micro/nanostructures, (b) the HRTEM image of ZnO netlike micro/nanostructures (inset: SEAD image of ZnO netlike micro/nanostructures), and (c) EDX spectrum of the ZnO netlike microstructures.

are very important for the application research in nano-optoelectronic and logic devices.⁶

The structure of the product on the Si substrate was determined by XRD. As shown in Figure 2, all of the diffraction peaks can be well indexed to the pure wurtzite structure of ZnO with lattice constants of $a = 3.249$ Å and $c = 5.206$ Å, which are consistent with the values in the standard card (JCPDS No. 36-1451). No diffraction peaks from any other impurities are detected.

To obtain more detailed structural information of the ZnO products, typical transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM)

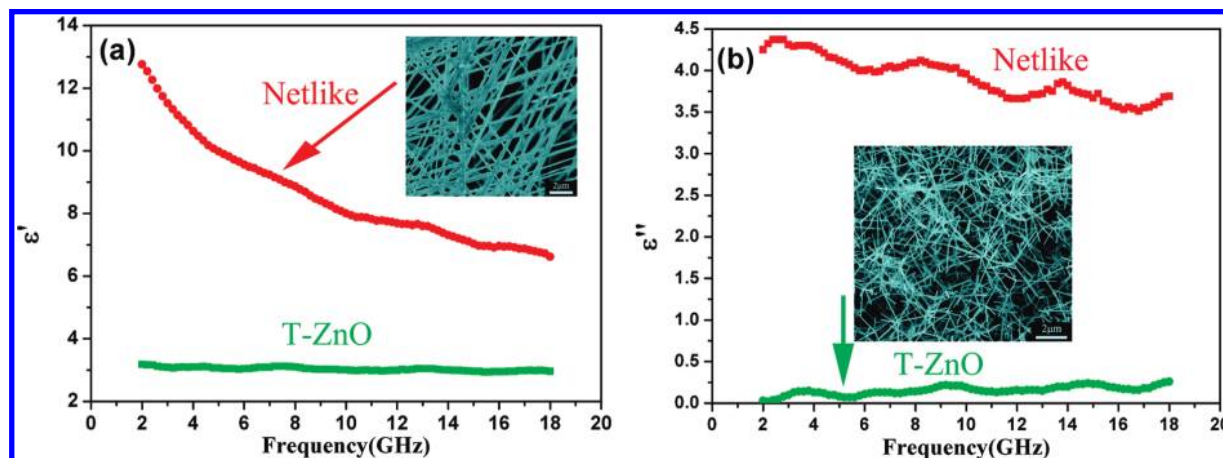


Figure 4. The frequency dependence of (a) real ϵ' and (b) imaginary ϵ'' parts of relative complex permittivity for ZnO nanotetrapod composite and netlike structures composite. The SEM image of ZnO netlike micro/nanostructures and T-ZnO nanostructures is shown in the inserts in panels a and b, respectively.

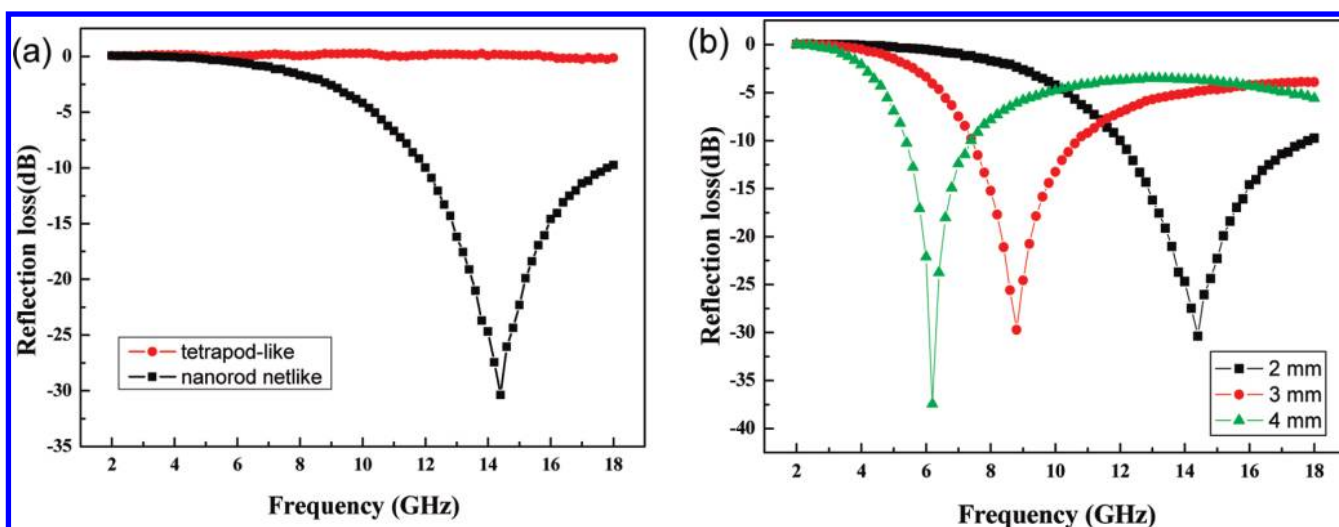


Figure 5. (a) Simulation of reflection loss of 50 vol % ZnO nanotetrapod and 50 vol % ZnO netlike micro/nanostructures composites with a thickness of 2.0 mm. (b) Simulation of reflection loss of 50 vol % ZnO netlikes micro/nanostructures composite of different thickness.

images are recorded, as shown in Figure 3. Figure 3a reveals a ZnO micro/nanorods bundle in the 3D networks. The individual ZnO nanorods have diameters in the range of 200–500 nm and a length of several micrometers. Figure 3b shows the HRTEM image and corresponding SAED pattern taken from the nanorod.

The HRTEM image of the fraction in Figure 3b clearly shows the lattice fringes with a d -space of 0.52 nm, which matches that of (0001) planes of the wurtzite structural ZnO. The inset of Figure 3b shows the corresponding SAED pattern taken from the nanorod. By combining HRTEM images with the corresponding SAED pattern, the growth direction of the fraction can be determined along [0001] and $[10\bar{1}0]$. It is noteworthy that the netlike structures, such as the TEM samples, are sufficiently stable, which cannot be destroyed even after ultrasonication for a long time. Therefore, these electron microscopy characterizations reveal the formation mechanism of ZnO netlike structure is following the V–S mode presented in the literature.^{17–19} The EDX spectrum (Figure 3c) exhibits that the sample is mainly composed of zinc and oxygen, and the obvious copper peaks are from the copper microgrid for HRTEM observation.

To investigate the microwave absorption property of netlike ZnO micro/nanostructures, the complex permittivity ϵ of the netlike micro/nanostructures was measured. For comparison, T-ZnO structures were also studied. Figure 4 shows the plots of the frequency versus the complex permittivity of the primary

ZnO netlike micro/nanostructures composites with 50 vol % ZnO netlike nanostructures (SEM image shown in the insert of Figure 4a) and T-ZnO composites with 50 vol % T-ZnO (see the insert in Figure 4b). The real permittivity of T-ZnO composite is about 3.1, and the imaginary permittivity is about 0.2 (corresponding green curve). However, for the ZnO netlike micro/nanostructures composite, the ϵ' and ϵ'' values show a complex variation (corresponding red curve). The real part of the relative permittivity (ϵ') declines from 15 to 6 in the frequency range of 2–18 GHz (Figure 4a). The imaginary part of the permittivity (ϵ'') decreases from 4.4 to 3.6 and the curve exhibits two broad peaks in the 7–9 and 12–15 GHz ranges (Figure 4b). It is worthy to notice that the peaks of the ϵ'' curve appear at 8 and 14 GHz, suggesting a resonance behavior, which is expected when the composite is highly conductive and skin effect becomes significant.¹⁴ The imaginary part ϵ'' of ZnO netlike micro/nanostructures is relatively higher in contrast to that of T-ZnO composites, which implies the distinct dielectric loss properties arising from the morphology variation. It is reasonable that the dielectric loss is attributed to the lags of polarization between the 3D frame interfaces as the frequency is varied. ZnO netlike micro/nanostructures possess more complicated interfaces than T-ZnO, resulting in better dielectric loss properties.¹⁴

To explain the microwave absorption properties of the samples measured above, the RL of the netlike micro/nanostructures and T-ZnO were calculated, respectively, using the relative complex permeability and permittivity at a given frequency and thickness layer according to the transmit-line theory, which follows the equations below:²⁰

$$Z_{\text{in}} = Z_0(\mu_r/\epsilon)^{1/2} \tanh[j(2\pi fd/c)(\mu_r\epsilon)^{1/2}] \quad (1)$$

$$\text{RL (dB)} = 20 \log |(Z_{\text{in}} - Z_0)/(Z_{\text{in}} + Z_0)| \quad (2)$$

where f is the microwave frequency, d is the thickness of the absorber, c is the velocity of light, Z_0 is the impedance of air, and Z_{in} is the input impedance of the absorber. The relative complex permeability and permittivity were tested on a network analyzer in the range 2–18 GHz. The simulations of the RL of the two composites with a thickness of 2.0 mm are shown in Figure 5a. The ZnO netlike micro/nanostructures composite possesses a strong microwave absorption property, the value of the minimum RL for the composite is −30 dB at 14.4 GHz. However, the T-ZnO composite has almost no absorption. Figure 5b shows simulations of RL of ZnO netlike micro/nanostructures composite with different thicknesses. The value of the minimum RL for the ZnO netlike micro/nanostructures composite is −37 dB at 6.2 GHz with a thickness of 4.0 mm. Compared with the previous report,¹⁰ in which the value of minimum RL for the composite with 50 vol % ZnO dendritic nanostructures is −25 dB at 4.2 GHz with a thickness of 4.0 mm, the ZnO netlike micro/nanostructures have more excellent properties.

About the mechanism of microwave absorption, Yan et al.¹⁴ explained the ZnO nanotrees microwaves absorption performances using isotropic antenna mechanism. The random distribution of the isotropic quasi-antenna ZnO semiconductive crystals not only leads to diffuse scattering of the incident microwaves, which results in the attenuation of electromagnetic (EM) energy, but also acts as a receiver of microwaves, which can produce vibrating microcurrent in the local networks. Here, in our experiment, we noted that the ZnO netlike structures have special geometrical morphology. Such isotropic crystal symmetry can form continuous isotropic antenna networks in the composites. Moreover, it is available for the EM wave to penetrate the nanocomposites formed by the numerous conductive ZnO networks, and the energy will be induced into dissipative current by random distributed isotropic antennas, and then part of the current will generate EM radiation and the rest will be consumed in the discontinuous networks, which lead to the energy attenuation. Thus, the tanglesome network frame of ZnO nanostructures in the composite will induce a certain extent of conductive loss. Compared with ZnO netlike micro/nanostructures, no complex frame exists in T-ZnO with the quasi-one-dimensional nanostructures the same as for the nanowire. A large part of EM radiation will counteract with each other when the orientation of these isotropic quasi-antennas distributes randomly. In a word, ZnO netlike nanostructures, acting as receiving antenna, can receive EM energy and transform it into dissipative current. And they also act as sending antenna

transforming the vibrating current into EM radiation. Besides these, the interfacial electric polarization should also be considered. The multi-interfaces between the isotropic antenna frame and air bubbles can benefit from the microwave absorption because of the interactions of EM radiation with charged multipoles at the interfaces.^{13,14}

4. Conclusions

In summary, the crossed ZnO netlike micro/nanostructures were successfully synthesized on a Si (001) substrate by controlling the growth conditions. The ZnO netlike micro/nanostructures/paraffin composites present the high performance of microwave absorption, and the value of minimum reflection loss for the composite with 50 vol % ZnO netlike micro/nanostructures and a thickness of 4.0 mm is −37 dB at 6.2 GHz. The unique morphology and excellent microwave absorption properties of 3D netlike ZnO structures suggest their potential application in functional electromagnetic shield devices.

Acknowledgment. This work was supported by the National Basic Research Program of China (Grant No. 2007CB936201), the Funds for International Cooperation and Exchange (Grant Nos. 50620120439 and 2006DFB51000), the Science Foundation (Grant Nos. 50772011, 20901010, and NCET-07-0066), and the Fundamental Research Funds for the Central Universities.

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JP100341H