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Anti-radar application of multiwalled carbon nanotubes and zinc oxide synthesized using a hydrothermal method

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Abstract

Anti-radar technology is essential to reinforce countries defense capacity. Previous studies have shown how the combination of a resistive material with a magnetic one is a good option for the development of radar absorbing materials. Multiwalled carbon nanotube (MWCNT)/ZnO material with MWCNT percentage variations of 1, 3, 5, and 7% has been proposed as a promising material in anti-radar technology. ZnO that is used in the synthesis of MWCNT/ZnO material resulting from a hydrothermal method was prepared using ZnSO4 and Na2CO3 as precursors. X-ray diffractograms show hexagonal phases for both MWCNT and ZnO, in the latter case hexagonal wurtzite. SEM analysis shows micrometer sheets for ZnO. The VNA test in the X-band frequency range (8 − 12.5 GHz) provides the reflection loss values. Based on the reflection loss value, MWCNT/ZnO material has an optimum absorption value of electromagnetic waves with a percentage of 3% MWCNT at a frequency of 11.2 GHz with an RL value of −31.4535 dB and a percentage of 7% MWCNT at a frequency of 11.2 GHz with an RL value of −25.3897 dB.

1. Introduction

The development of radar technology in the military field is very important in supporting national defense. This is caused by reflections of electromagnetic waves that hit the object’s target conductor and are detected by the opponent’s radar machine so that attacks can be easily carried out against the detected object. Overcoming this problem can be achieved by fooling the opponent’s radar so that it cannot find the position of the target object, using radar absorbing material (RAM) in the form of material absorber [1−4]. The RAM material capacity depends on the combination between electrical and magnetic losses, and a good microwave absorbing material should fulfill the requirements of high reflection loss coefficient (RL) and being lightweight and of low thickness. A wide variety of investigations have focused on carbon-based materials, ceramic materials, magnetic nanomaterials and other compounds [5−8].

Zinc oxide (ZnO) can be used as an anti-radar material because it is classified as a semiconductor material. ZnO has a resistivity value of 0.62−0.65 × 10³ Ω m. There are several precursors that can be used such as Zn(OH)2 used by Liu, et al [9], Zn(NO3)2 used by Greene J F, and Fraser S, [10] and ZnSO4 used by Wen, et al [11] and Ristiawan, et al [12]. Some methods that have been used to make ZnO are chemical vapor deposition (CVD), laser ablation, solution, and hydrothermal methods. The hydrothermal method has several advantages, namely using a low temperature, a simple manufacturing process, and the obtained results have high purity [13].

In the study by Liu et al [9] in increasing microwave absorption, ZnO powder was mixed with MWCNT at a certain percentage using a simple mechanical mixing method. The minimum reflection loss of −37.03 dB at 12.24 GHz occurs at the sample with addition of 4% MWCNT. Based on the research by Zhao et al [13], the reflection loss of Ag nanowire-filled MWCNT/epoxy composites has a minimum value of −19.19 dB at 7.8 GHz.

The ZnO used is the result of hydrothermal synthesis using ZnSO4 and Na2CO3 as precursors as used in the research by Ristiawan [12].
The purpose of this study is to analyze the influence of structure and morphology of MWCNT composition variation on ZnO and analyze the effect of microwave absorption from MWCNT composition variation on ZnO.

2. Experimental

The material used in this research is an MWCNT made using the method of spray pyrolysis and ZnO from the hydrothermal method. ZnO was synthesized with ZnSO₄ and Na₂CO₃ as precursors. The homogeneous mixing of MWCNT and ZnO was done mechanically.

Preparation is done for testing using a Vector Network Analyzer (VNA) to determine the value of the return loss. The experiment consisted of four samples, a mixture of MWCNT and ZnO with MWCNT compositions of 1, 3, 5 and 7%. The sample was then printed on an acrylic mold with a size of 21 mm × 10 mm × 2 mm. This measure corresponds to the waveguide size on the VNA for the frequency range of 8–12.5 GHz (x-rays).

The data obtained in the measurements were processed before being discussed further. The analysis of the four MWCNT/ZnO samples includes study of the crystal structure by x-ray diffraction, surface morphology analyzed using a scanning electron microscope (SEM) and reflection loss analyzed using VNA.

The VNA is first calibrated at the connector calibration plane and the material under test (MUT) is placed in a sample holder. The MUT must fit tightly in the sample holder in order to reduce the measurement uncertainty caused by air gaps. The calibration plane can be extended to the sample surface by two methods [14].

The reflection coefficient can be measured through the energy reflected by the surface covering the steel and compared with the energy reflected by the steel itself without any coating [14]. The reflection coefficient has a relationship with the s-parameter, where the s-parameter is a complex value of the impedance generated using the port network by VNA [15].

S-parameters are defined as the following matrix:

\[
S = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix}
\]

(1)

In measuring the impedance value of the reflection coefficient (\(\Gamma\)) which has a relationship with the s-parameter [16], it is formulated as follows:

\[
\Gamma = X \pm \sqrt{X^2 - 1},
\]

(2)

where

\[
X = \frac{S_{11}^2 - S_{21}^2 + 1}{2S_{11}}.
\]

(3)

The decibel (dB) measurement of the reflection coefficient can be stated in the following equation:

\[
Rc \text{ (dB)} = -20 \log |\Gamma|.
\]

(4)

Return loss analysis is used to find out how much power is lost and not reflected back to the receiver. The most expected condition for the best return loss is less than –10 dB. Return loss is expressed in the following equation:

\[
R_L = -20 \log |\tau|,
\]

(5)

where

\[
\tau = S_{11} - \frac{S_{12}S_{21}}{1 + S_{22}}.
\]

(6)

\(\tau\) is return loss in the form of impedance value and \(R_L\) is the return loss value in the form of dB [15–17].

3. Results and discussion

3.1. Morphological analysis of MWCNT/ZnO

The MWCNT/ZnO material was synthesized using hydrothermal ZnO powder precursors, based on research by Ristiawan, et al (2018), which was physically white and the MWCNT powder produced using the spray pyrolysis method, which was physically black. Synthetic MWCNT/ZnO is made by mixing manually with a composition of MWCNT in a sequence, i.e., 1%, 3%, 5%, and 7%. The results are produced physically in the form of gray powder.
3.2. XRD analysis of MWCNT/ZnO

XRD testing was done with an angle range of \(2\theta \) equals 20°–90° using a CuK\(\alpha\) wavelength of 1.54 Å. The XRD test results were then identified using the Match! 3 Software using open database crystallography (COD) as a reference.

Figure 1 presents the x-ray diffraction (XRD) patterns of synthesized powder. The peak positions in each product agree well with the reflections of MWCNT/ZnO materials with all peaks corresponding well to standard crystallographic data based on references COD9012230, COD9012231, and COD2300114 [18, 19]. As could be seen from the XRD patterns, all products have polycrystalline nature and peaks belonging to the (102), (110), (100), (002), (101), (110), (103), and (112) reflections were seen in ZnO, also (002) and (100) reflection for C.

3.3. SEM analysis of MWCNT/ZnO

The mixing of the ZnO material in sheet form resulting from the hydrothermal process with MWCNT in the mechanical milling process produces the morphology as shown in the figure 2. The milling treatment in this mixing process causes some of the ZnO to become agglomerated. However, the result of this mixing causes ZnO to cover MWCNT and this can be used to absorb electromagnetic waves.

3.4. Electromagnetic wave absorption analysis

In analyzing the absorption of electromagnetic waves, several parameters are used, namely, reflection loss. The reflection loss analysis is used to determine the absorption ability of materials against electromagnetic waves by MWCNT/ZnO.
Figure 3 shows the value of reflection loss in MWCNT/ZnO materials with MWCNT composition of 1, 3, 5 and 7%. The minimum reflection loss is $-31.4535$ dB at 11 GHz with MWCNT composition of 3%.

There are two frequency points with optimum absorption values of 9.5 and 11 GHz which are described in Table 1.

Based on research by Liu et al. (2012) with MWCNT composition of 4%, the optimum reflection loss value is $-18.91$ dB at 10.96 GHz. In this research, we have obtained a smaller reflection loss value at frequency of 11 GHz than that produced by Liu et al. in all of MWCNT compositions.

The MWCNT can absorb the electromagnetic energy and attenuate the radiation via the interaction between interior electrons and exterior electromagnetic radiation. It has been reported that the defects in MWCNT can act as polarization centers and contribute to strong electromagnetic absorption, which is mainly attributed to the dielectric relaxation [20].

MWCNT has been developed for the purposes of electromagnetic wave absorption. Reports from the literature specifically investigating the propensity for dielectric and magnetic interaction of materials as a function of particle size have reported that, as the size of particulate matter is constrained, electromagnetic interaction tends to increase. Study the intrinsic effects of dielectric and magnetic MWCNT for electromagnetic absorption don’t explicitly investigate their materials as a function of particle size, but nevertheless, the particle size parameter does appear to constitute an important factor when it comes to utilizing these MWCNT for electromagnetic interference shielding and electromagnetic absorption [21].

The ferromagnetic properties are believed due to the residual ferromagnetic substances from the MWCNT fabrication processes. The observed high frequency permeability properties were also thought to be due to the ferromagnetic impurities in MWCNT and SWCNT. The microwave absorption properties of MWCNT are better than SWCNT in terms of reflection loss (RL) and absorption bandwidth [22]. Spray pyrolysis method to produce MWCNT material will leave Fe impurity originating from ferrocene catalyst. Although MWCNT has refluxed to remove Fe, the result of MWCNT reflux still leaves Fe. Figure 4 shows the energy dispersion X-ray results of MWCNT after reflux treatment which is used as electromagnetic wave absorber in this study.

| Composition of MWCNT | Frequency 9.5 GHz | Frequency 11 GHz |
|----------------------|-------------------|-----------------|
| 1%                   | $-21.8373$ dB     | $-19.8737$ dB   |
| 3%                   | $-18.6795$ dB     | $-31.4535$ dB   |
| 5%                   | $-22.0204$ dB     | $-18.4888$ dB   |
| 7%                   | $-16.4453$ dB     | $-25.3897$ dB   |

Figure 3. Reflection loss of MWCNT/ZnO materials with MWCNT composition of 1, 3, 5 and 7%.

Table 1. Value of minimum reflection loss of MWCNT/ZnO materials with MWCNT composition of 1, 3, 5 and 7%.
4. Conclusion

Synthesis of MWCNT/ZnO material can be performed by mixing manually, which results in a gray powder. Analysis of the XRD test results showed the presence of hexagonal MWCNT types and hexagonal wurtzite-type ZnO. SEM image analysis shows that sheet-type ZnO is formed. The VNA test analysis results obtained based on reflection loss values show that the MWCNT/ZnO material has the optimum absorption value of electromagnetic waves with 3% MWCNT at a frequency of 11.2 GHz with an RL value of $-31.4535\,\text{dB}$ and 7% MWCNT at a frequency of 11.2 GHz with an RL value of $-25.3897\,\text{dB}$.

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