MOCVD Growth of Fe Thin Films on SrFe12O19 Surface and Their Microwave Absorption Properties Postprint

Authors: Liu Yuan, Liu Xiangxuan, Wang Xuanjun, Chen Xin

Date: 2016-11-04T00:00:00+00:00

Abstract

Using metal-organic chemical vapor deposition (MOCVD) process, with high-purity Fe(CO)5 and SrFe12O19 as raw materials and high-purity N2 as carrier gas, a continuous Fe film was deposited on the SrFe12O19 surface to prepare SrFe12O19 @ Fe composite materials. The structure and electromagnetic properties of the powder were characterized by X-ray diffractometer, scanning electron microscope, energy dispersive spectrometer, and vector network analyzer, and its microwave absorption performance was investigated. The results demonstrate that the deposited film on the SrFe12O19 surface is pure α-Fe phase with a thickness of approximately 0.5 m, and the film covers the SrFe12O19 surface relatively uniformly and completely; after depositing the α-Fe film on the SrFe12O19 surface, its electromagnetic properties changed significantly, and the microwave absorption capability was substantially improved. The sample prepared with a deposition time of 30 min exhibited optimal microwave absorption performance; when the coating thickness was 1.5–3 mm, the minimum reflection loss was below -19 dB, and microwave absorption intensity below -10 dB was achieved in the 6.8–18 GHz frequency range. As the thickness increased, the minimum reflection loss first decreased and then increased; at a thickness of 2.0 mm, it reached -21.2 dB at 11.6 GHz.

Full Text

Fe Thin Films Grown on SrFe12O19 Surface by MOCVD Method and Their Microwave Absorption Properties

LIU Yuan, LIU Xiangxuan, WANG Xuanjun, CHEN Xin

No. 603 Faculty, Xi'an Research Institute of High Technology, Xi'an 710025

Abstract

Using metal organic chemical vapor deposition (MOCVD) with high-purity Fe(CO)5 and SrFe12O19 as precursors and high-purity N2 as carrier gas, continuous Fe films were deposited on SrFe12O19 surfaces to fabricate Fe-SrFe12O19 composite materials. The structure, morphology, and electromagnetic properties of the powders were characterized using XRD, SEM, EDS, and a vector network analyzer, and their microwave absorption performance was investigated. The results demonstrate that the deposited film on the SrFe12O19 surface consists of pure α-Fe phase with a thickness of approximately 0.5 m, forming a relatively uniform and complete coating over the SrFe12O19 surface. After α-Fe film deposition, the electromagnetic properties of SrFe12O19 changed significantly, with notable improvement in microwave absorption performance. The sample prepared with a deposition time of 30 min exhibited optimal absorption properties. For coating thicknesses of 1.5-3 mm, the minimum reflection loss was below -19 dB across the entire 6.8-18 GHz range. As thickness increased, the reflection loss peak first decreased then increased, reaching a minimum value of -21.2 dB at 11.6 GHz for a thickness of 2.0 mm.

Keywords: carbonyl iron, MOCVD, electromagnetic properties, microwave absorption

Introduction

With the rapid development of the electronics industry, electromagnetic radiation has become a new form of environmental pollution, and its interference with electronic equipment and potential hazards to human health have attracted widespread attention from researchers. Currently, electromagnetic shielding and anti-interference technologies serve as the primary means of protection, making the study of microwave absorbing materials a hot research topic. In fundamental research on absorbing materials, developing high-performance absorbing agents is crucial. SrFe12O19 is widely used in electromagnetic wave absorption materials due to its large magnetic anisotropy, high coercivity, and stable chemical properties. Carbonyl iron (CI) has been extensively applied in microwave absorbing materials because of its simple preparation process, low cost, and large magnetic loss angle. Additionally, CI exhibits good dielectric properties at high frequencies, allowing effective tuning of electromagnetic parameters by adjusting its content in composites.

Currently, few studies have investigated the growth of micro/nano metal shells on SrFe12O19 surfaces. Pan et al. coated SrFe12O19 with various magnetic metals via electroless plating and found that the microwave absorption properties of magnetic metals and SrFe12O19 are complementary. The unique core-shell structure or interfacial interactions between core and shell also contribute to electromagnetic wave absorption. Our previous research modified SrFe12O19 through Nd-Co and La-Co doping and deposited Fe films on La-Co modified powders, which improved microwave absorption performance. However, rare earth elements are expensive, limiting practical applications. Therefore, it is necessary to develop a one-step reaction method for direct Fe thin film deposition on SrFe12O19 surfaces.

This work employs metal organic chemical vapor deposition (MOCVD) using high-purity Fe(CO)5 and SrFe12O19 as raw materials and high-purity N2 as carrier gas to design and chemically modify composite microwave absorbing agents at the micro/nano scale, preparing Fe-SrFe12O19 composite materials and investigating their microstructure and electromagnetic properties.

1 Experimental Materials and Methods

SrFe12O19 powder was synthesized via a sol-gel method. Analytical-grade Sr(NO3)2 and Fe(NO3)3 were weighed according to the stoichiometric ratio of SrFe12O19 and dissolved in deionized water. Citric acid with the same molar mass as the metal ions was added, and the solution was stirred for 30 min to form a homogeneous transparent solution. While continuously stirring, 25% NH3 · H2O was added dropwise to adjust the pH to 7. The beaker containing the solution was placed in a water bath at 80 °C and continuously stirred until a viscous wet gel formed. The wet gel was transferred to a drying oven at 120 °C to obtain a brownish-yellow dry gel, which was then ignited on an electric furnace to produce SrFe12O19 precursor powder. The precursor powder was heat-treated at 1000 °C for 3 h (heating/cooling rate of 5 °C/min, with natural cooling after reaching 300 °C) to obtain SrFe12O19 powder.

For the MOCVD process, 5 g of SrFe12O19 powder and 15 mL of iron pentacarbonyl [Fe(CO)5] were placed in the reactor and evaporator, respectively. N2 gas was introduced to purge air from the pipeline, after which the gas source and the valve between reactor and evaporator were closed. When the SrFe12O19 and Fe(CO)5 reached 180 °C and 80 °C, respectively, the valve between reactor and evaporator was opened, and N2 at 30 mL/min flow rate carried Fe(CO)5 vapor into the reactor. Continuous stirring during the reaction ensured uniform Fe coating on SrFe12O19 surfaces. The N2 flow rate was controlled by a gas flow meter, while Fe(CO)5 was heated using an HH-SA digital constant-temperature oil bath. Pipelines before the reactor were wrapped with insulation to prevent Fe(CO)5 condensation at low temperatures. Deposition times of 10, 30, and 60 min were used, and samples were cooled and collected under N2 protection.

Phase analysis was performed using a Rigaku D/max-2400X X-ray diffractometer (XRD) with Cu Kα radiation ($\lambda = 0.15418$ nm) at 40 kV and 100 mA, using step scanning with a step size of 0.02° and scan rate of 15 °/min over a 2 range of 15°–80°. Sample morphology was examined using a VEGA II XMU INCN scanning electron microscope (SEM), and elemental distribution was analyzed using an INCA 7718 energy dispersive spectrometer (EDS). Electromagnetic parameters were measured using an HP-8720ES vector network analyzer with a coaxial method. Test samples were prepared with paraffin as matrix (40 wt% paraffin, 60 wt% absorbent) following the method in reference [3]. Microwave absorption performance was evaluated using the RAM reflection arch measurement method with epoxy resin as matrix and polyamide as curing agent (60 wt% absorbent), following the coating preparation method in reference [9].

2.1 XRD Analysis

[Figure 1: see original paper] shows XRD patterns of Fe-SrFe12O19 samples prepared at different reaction times. Comparison with standard SrFe12O19 and α-Fe patterns reveals that all samples exhibit distinct α-Fe characteristic peaks around 2 = 44.5°. As deposition time increases, SrFe12O19 characteristic diffraction peaks gradually weaken while the α-Fe (110) orientation at 44.5° strengthens. Using Jade 5.0 software with the RIR method, the relative α-Fe contents in the 10, 30, and 60 min samples were calculated to be 11%, 20%, and 26%, respectively.

2.2 SEM Analysis

[Figure 2: see original paper] presents SEM images of SrFe12O19 and Fe-SrFe12O19 powders at different deposition times. The as-prepared SrFe12O19 shows well-defined crystal structures with relatively perfect hexagonal shapes. When the reaction time is too short (10 min), the amount of Fe produced is relatively small with fine dispersed particles, resulting in incomplete SrFe12O19 surface coverage. As deposition time increases (30–60 min), Fe particles gradually form continuous dense films from dispersed granular arrangements, completely covering SrFe12O19 particle surfaces with increasing shell thickness, indicating that Fe yield increases with reaction time within this period.

Samples were cold-mounted with epoxy resin, ground, and polished for cross-sectional SEM observation and EDS analysis. [Figure 3a: see original paper] clearly shows the sample cross-section with a continuous bright material coating the SrFe12O19 particles, allowing clear distinction between the α-Fe shell and SrFe12O19 core based on color contrast. Shell thickness measurements using an electronic scale indicate an average thickness of approximately 0.5 m. [Figure 3b: see original paper] shows EDS analysis of the sample shell, confirming the coating is elemental Fe based on Fe, Sr, and O distribution patterns combined with XRD results, demonstrating successful fabrication of core-shell structured Fe-SrFe12O19 powder.

2.3 Electromagnetic Parameter Analysis

[Figure 4: see original paper] shows the complex permittivity (’, ”) and complex permeability (’ , ”) of Fe-SrFe12O19 at different reaction times. As reaction time increases, both the real (’) and imaginary (”) parts of complex permittivity gradually increase, showing substantial improvement compared to pure SrFe12O19. Combined XRD and SEM analyses indicate that increasing deposition time leads to thicker α-Fe shells with higher content, enhancing dielectric loss and resulting in increased complex permittivity. The real part of permeability (’) of coated samples exceeds that of uncoated SrFe12O19 and increases with deposition time, reaching a maximum at 60 min. However, the imaginary part of permeability (”) decreases with increasing deposition time. SrFe12O19 exhibits a resonance loss peak in ”between 5-7 GHz, which disappears in coated samples. While SrFe12O19 shows higher ” than all coated samples in the 2-7 GHz range, its ” becomes lower than coated samples in the 11-18 GHz range.

In the microwave frequency band, dielectric loss originates from self-polarization and interfacial polarization. The numerous interfaces between SrFe12O19 and α-Fe provide enhanced interfacial polarization, thereby increasing dielectric loss. Magnetic loss in microwave magnetic materials primarily results from eddy current loss, magnetization vector rotation, natural resonance, and domain wall resonance. Magnetization vector rotation only occurs under strong magnetic fields, while domain wall resonance occurs in multi-domain materials. Therefore, magnetic loss in Fe-SrFe12O19 mainly arises from natural resonance and eddy current loss. If magnetic loss originated solely from eddy current loss, the value of f^{-1}(’)$^{-2}$ ’ ’ would remain constant with frequency variation. [Figure 5: see original paper] shows the relationship between f^{-1}(’)$^{-2}$ ’ ’ values and frequency for Fe-SrFe12O19, demonstrating a decreasing trend with increasing frequency, thus confirming that natural resonance dominates the magnetic loss mechanism.

Effective microwave absorption requires two conditions: first, electromagnetic waves must penetrate the material interior as much as possible (good impedance matching), and second, the material must effectively dissipate the incident waves (large attenuation constant α). Since ferrite materials exhibit good electromagnetic matching properties, enhancing their wave dissipation capability becomes particularly important. Analysis of [Figure 6: see original paper] reveals that the attenuation constant α significantly increases after Fe film growth on SrFe12O19 surfaces, indicating superior microwave absorption performance of Fe-SrFe12O19 compared to pure SrFe12O19. The sample prepared with 30 min deposition time shows a relatively large attenuation constant.

2.4 Microwave Absorption Performance Analysis

Based on transmission line theory and measured electromagnetic parameters, the reflection loss of SrFe12O19 and the 30 min deposition sample was calculated. The results are shown in [Figure 7: see original paper]. When using SrFe12O19 alone as absorbent, the matching thickness is large (approximately 5 mm) with few matching points and poor absorption performance. Using Fe-SrFe12O19 as absorbent significantly improves absorption performance with reduced matching thickness and multiple matching points at different thicknesses.

To more intuitively reflect the absorption effectiveness of Fe-SrFe12O19, reflection loss was calculated for thicknesses between 1.5-3.0 mm, as shown in [Figure 8a: see original paper]. As thickness increases, the reflection loss peak gradually shifts to lower frequencies according to the relationship:

$$f_m = \frac{c}{2\pi d}\sqrt{\frac{\mu''}{\varepsilon'}}$$

where f_m is the matching frequency, c is the speed of light in vacuum, d is thickness, and μ'' is the imaginary part of complex permeability. This demonstrates that increased thickness causes f_m to shift toward lower frequencies. The reflection loss peak first decreases then increases with thickness, reaching a minimum value of -21.2 dB at 2.0 mm thickness. For thicknesses between 1.5–3.0 mm, the minimum reflection loss remains below -19 dB, with an effective bandwidth of 11.2 GHz (6.8–18 GHz) where reflection loss is less than -10 dB.

A coating with the optimal 2.0 mm thickness was prepared and tested, with results shown in [Figure 8b: see original paper]. Although some discrepancy exists between experimental and theoretical values, the experimental results generally reflect the theoretical optimization. This error likely arises from using paraffin as matrix for electromagnetic parameter measurement versus epoxy resin for actual coatings, possible thickness variations between theoretical and actual coatings, and non-ideal coating surface conditions.

Conclusions

1. At a deposition temperature of 180 °C, deposition time of 30 min, and carrier gas flow rate of 30 mL/min, a uniform Fe thin film with average thickness of 0.5 m forms on SrFe12O19 surfaces, successfully fabricating core-shell structured Fe-SrFe12O19 composite powder.
2. Fe film deposition on SrFe12O19 surfaces significantly alters electromagnetic parameters. The numerous interfaces between SrFe12O19 and Fe provide enhanced interfacial polarization, increasing dielectric loss, while magnetic loss in Fe-SrFe12O19 composite powder is dominated by natural resonance.
3. The sample prepared with 30 min deposition time exhibits optimal absorption performance. For coating thicknesses of 1.5-3 mm, the minimum reflection loss remains below -19 dB, achieving absorption intensity below -10 dB across 6.8-18 GHz. As thickness increases, the reflection loss peak first decreases then increases, reaching a minimum of -21.2 dB at 11.6 GHz for a 2.0 mm thickness.

References

[1] Huang Y B, Qian J S, Zhang J Y. J Chin Coal Soc, 2010; 35: 135

[2] Hirata A, Morita M, Shiozawa T. IEEE T Electromagn, 2003; 45C: 109

[3] Liu Y, Liu X X, Wang X J, Zhang Z Y, Li R, Guo L. Chin J Nonferrous Met, 2013; 23: 168

[4] Zhou J, Yu W, Xun Z G, Gong J G. Acta Metall Sin, 2010; 46: 967

[5] Liu Y, Liu X X, Wang X J, Chen X. J Chin Ceram Soc, 2013; 41: 755

[6] Wang Y F, Li Q L, Zhang C R, Jing H X. J Alloys Compd, 2009; 467: 284

[7] Yao X B, Hu G G, Yin P, Fang Q Q, Lv Q R. Funct Mater, 2002; 33: 633

[8] Jing H X, Li Q L, Ye Y, Yang X F. Acta Mater Comp Sin, 2013; 30: 130

[9] Liu Y, Liu X X, Wang X J. J Alloys Compd, 2014; 584: 249

[10] Zhou J, Wang W, Sun Z G, Gong J G. Acta Metall Sin, 2010; 46: 967

[11] Tong G X, Gong J G, Zhang W Y, Zhang W, Wang W, Dong D M. Acta Metall Sin, 2008; 44: 1001

[12] Liu Y, Liu X X, Wang X J, Wen W. Chin Phys Lett, 2014; 31: 047702

[13] Cheng Y L, Dai J M, Wu Y P. J Magn Magn Mater, 2010; 32: 97

[14] Pan X F, Mu G H, Shen H G, Gu M Y. Appl Surf Sci, 2007; 253: 4119

[15] Pan X F, Shen H G, Qiu J X, Gu M Y. Mater Chem Phys, 2007; 101: 505

[16] Pan X F, Shen H G, Qiu J X, Gu M Y. J Mater Sci: Mater Electron, 2007; 42: 2086

[17] Zhang Z Y, Liu X X, Wang X J, Wu Y P, Liu Y. J Magn Magn Mater, 2012; 324: 2177

[18] Zhang Z Y, Liu X X, Wang X J, Wu Y P, Rong L. J Alloys Compd, 2012; 525: 114

[19] Zhang S Y, Cao Q X. Mater Sci Eng, 2012; 177B: 678

[20] Liu Y, Liu X X, Chen X, Wang X J. J Inorg Mater, 2013; 28: 1328

[21] Yang Y, Xu C L, Xia Y X, Wang T, Li F S. J Alloys Compd, 2010; 493: 549

[22] Zhang B S, Feng Y, Xiong J, Yang Y, Lu H X. IEEE Trans Magn, 2006; 42: 1778

[23] Naito Y, Suetake K. IEEE Trans Microwave Theory Technol, 1971; 19: 65

[24] Meshram M R, Agrawal N K, Sinha B, Misra P S. J Magn Magn Mater, 2004; 271: 207

[25] Maeda T, Sugimoto S, Kagotani T, Tezuka N, Inomata K. J Magn Magn Mater, 2004; 281: 195

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.