# Nanocrystalline Ferromagnetic Microwires Silicone Flexible Composite With Optical Transparency

Lie Liu, *Member, IEEE*, Zhi Hong Yang, Ling Bing Kong, and Ping Li

***Abstract*—Novel flexible transparent composite sheets were fabricated with glass-coated nanocrystalline ferromagnetic microwires and transparent silicone matrix. The free-space method was employed to measure the effective permittivity and shielding effectiveness (SE) of samples fabricated from 4 to 20 GHz. SE of the transparent shielding layer with 1wt% of microwires and thickness of 0.85 mm can be more than 20 dB when frequency is above 11 GHz. Due to resonance phenomena of the embedded shortcut microwires with a length of about 5 mm, both dielectric permittivity and loss of the composite are quite high at microwave frequency. Hence, such transparent composite sheets may also find applications in microwave applications**

***Index Terms*—Composites, ferromagnetic microwire, shielding effectiveness (SE), wave absorption.**

## I. INTRODUCTION

WITH the growth of the wireless communications and the global position system, the working frequency of consumer electronics has been shifted to gigahertz range. Electromagnetic shielding or absorbing materials with higher working frequency is needed to reduce electromagnetic (EM) interference among different devices, and also to protect confidential information. Current EM shielding materials include thin metallic films, fibers, flakes, and composite coatings with conductive fillers, like silver nanoparticles, carbon black or carbon fibers, etc.

For window and dome applications with requirement of high optical transparency, indium tin oxide (ITO)-deposited polymer film has been proposed to shield incident EM wave for wireless applications [1], [2]. It was found that transmission coefficient is about −25 dB at 60 GHz [1] and the calculated reflection loss can be up to 50 dB [2]. Similar transparent ITO film achieved more than 17 dB absorption also at the frequency range between 8.3 and 11.6 GHz [3]. Shielding effectiveness (SE) of multilayered thin films with ITO and silver deposited alternately was measured from 50 MHz to 1.5 GHz [4]. The minimum transmittance to optical light was about 60% and the SE measured was over 50 dB, which is close to the theoretical calculation also [4]. However, ITO-based transparent shielding layers need to have certain thickness and well-designed multilayer structure. This, together with the material itself, result in high cost.

In the last few years, more attention has been paid to development of transparent shielding composites of carbon particles with size of few nanometers, such as carbon nanotube (CNT) and graphene [5]–[7]. It was reported that single-walled CNT could be used to fabricated films with SE of 43 dB at 10 MHz and 28 dB at 10 GHz were found with 90% optical transmittance, which suggests that they could be promising transparent microwave shielding material [5]. CNT and polyurethane composite films may also have good light transparency [7]. However, they may not have high EM SE due to their extremely small thickness. Also, the light transparency could be compromised if the thickness is too large or the concentration of CNTs is too high.

EM shielding composites based on commercial continuous stainless steel and carbon fiber embedded polymethylmethacrylate matrix could have SE more than 10 dB at 21 GHz and good transparency [8]. Glass-coated ferromagnetic microwires have nanocrystalline cores and transparent glass shell. Their transparency to visible light and corrosive-resistance performance are better than bare metal wires. Also, the unique structure and magnetostriction effect of microwires render them extremely high magnetic permeability at high frequency [9]. It is well known that high permeability could reduce the skin depth of fibers. Hence, such microwires with very small thickness could be sufficient for shielding or absorbing purposes. EM shielding properties of composite embedded with continuous microwires at 1–2 GHz was investigated, and SE of 18 dB was obtained from the composite layer with very low loading of 0.024% by volume and thickness of 0.64 mm [10].

Continuous microwires can be used in long-fiber reinforced composites or weaving structures. However, continuous microwires are not suitable for coating or molding methods that are among the most commonly used fabrication methods. In this paper, we report on fabrication and characterization of novel transparent shielding sheets embedded with shortcut glass-coated microwires. The microwires were first mixed with transparent silicone precursor by mechanical mixer and composite sheets were then prepared with molding method. Effective permittivity and shielding properties of the transparent microwire composites were evaluated and discussed based on the results from free-space measurement.

## II. FABRICATION AND CHARACTERIZATION

Casting (Taylor–Ulitovsky) method [11] was used to fabricate glass-coated microwires with different components and

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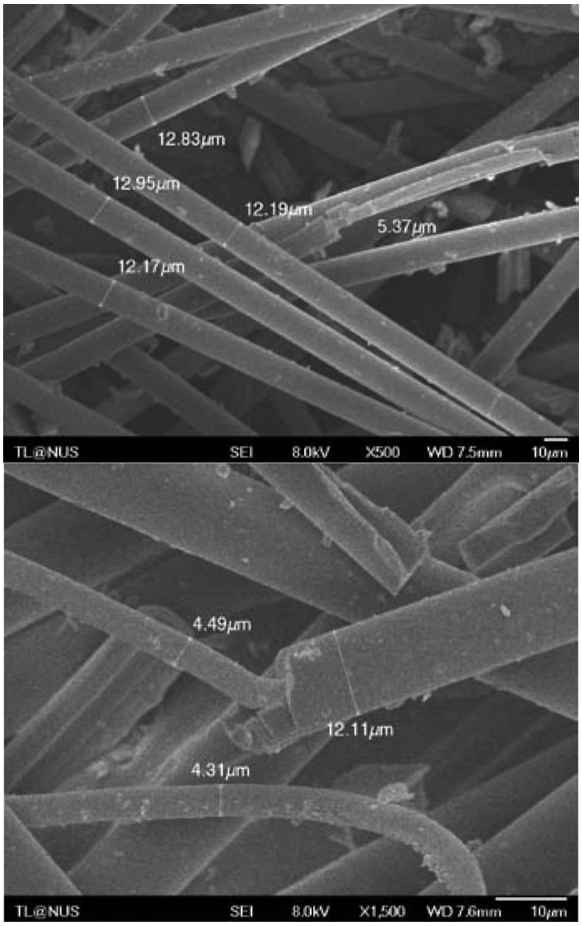

Fig. 1. SEM image of the microwires.

structures of metallic nucleus. The microwires consisted of an inner metallic nucleus covered by a Pyrex-like glass shell. The compositions of the alloy and the process parameters (including casting rate and cooling rate) determine the microstructure and geometrical characteristics, as well as static and dynamic magnetic behaviors of the microwires and their composites [12]. This method is able to control and adjust the geometrical parameters of the microwires during fabrication. It also produces microwires with repeatable properties at mass production [12].

Geometry and dimension of the microwires were examined by using JOEL JSM-6701F field emission scanning electronic microscope (SEM). As shown in Fig. 1, CoFeNiSiB microwires with average outer diameter of 12.5 $\mu$m and inner diameter of 5 $\mu$m were prepared with the casting method stated previously. Phase composition and crystalline structure of the microwire were characterized by using an X-ray diffraction (XRD) (Rigaku Ultima IV with Cu K$\alpha$ radiation and $\lambda = 1.54056$ A). Slow scan rate (1°/min) could increase the resolution of the minor peaks. The voltage and current applied to X-ray radiation source are 40 kV and 40 mA, respectively. Vibrating sample magnetometer (VSM, ADE Magnetics EV-7) was employed to measure hysteresis loop of the microwires with external field up to 2.1 T. Coercivity $H_C$ and saturation magnetization $M_S$ were obtained from the hysteresis loops measured.

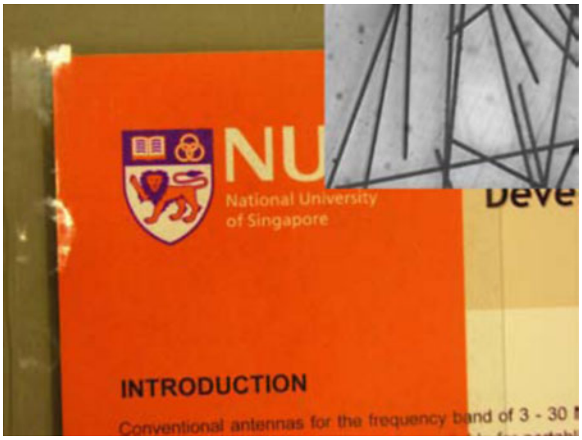

Fig. 2. Photographs of microwire composite sheet with 0.2wt% of microwire filler taken with camera and microscope.

Continuous microwires were cut into 5-mm-long microfiber with paper cutter. The tolerance of the fiber length is less than 0.2 mm. Then, the microfibers were mixed with Sylgard 184 silicone elastomer (Dow Corning Corporation, Midland, MI) by using a mechanical mixer for 30 min. To avoid any further damage to the microfibers and their glass coatings, stirrer made of Teflon instead of the steel one was used and the stirring speed was limited at 60 r/min. It was found that due to their large size and thin thickness, high-speed mixing or ultrasonication processing would break the microfiber into smaller pieces which compromised the shielding performance of the final products. The mixture was then cast into a stainless steel mould. Special care needs to be taken to avoid any air bubbles and voids during the sample preparation. The mould was then screwed up before being cured on hotplate at 150 °C for 1 h. As shown in Fig. 2, the prepared silicone rubber sheet has fairly good transparency to optical light. Picture of the embedded microwires was also taken by using optical microscope. The embedded microwires were dispersed inside the silicone matrix uniformly and could hardly be seen by naked eyes.

To understand the effect of fiber distribution and length, we have prepared a composite with continuous regular microwires parallel to the incident electrical field (regular composite in short). The length of microwires is the same as the size of the composite sheet, 20 cm. The spacing of neighboring microwires is 5 mm.

## III. FREE-SPACE MEASUREMENT

Free-space setup shown in Fig. 3 includes a pair of broadband transmitter and receiver antennas (Flann DP240 dual polarized horn) with working frequency from 4 to 20 GHz [13]. They are connected to vector network analyzer (VNA), Agilent N5230A by a pair of phase-stable cables. Both transmitter/receiver antennas and an Acrylic sample holder were fixed to the Acrylic base. The distance from antennas to sample is 75 cm. Hence, the measurement is carried out in the near-field zone. A hole with diameter of 16 cm is cut at the center of the sample holder that was covered with broadband absorber from both sides. Since the size

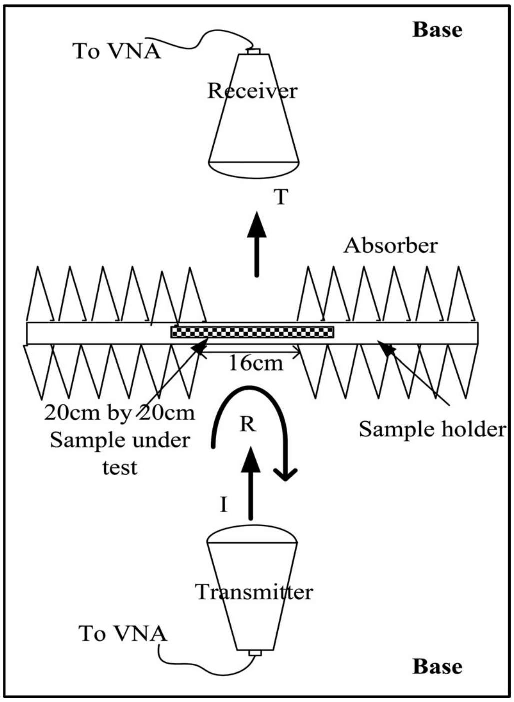

Fig. 3. Free-space setup.

of the sample (20 cm × 20 cm) is larger than the hole, the diffraction from edges of the sample can be minimized effectively by the absorber. As for multiple reflections, gated reflection line (GRL) was used to cut the signal with longer delay time from that through the sample. The noise from environment and leakage power could be effectively removed according to the improved method for performing a full two-port parameter calibration in free-space reported in [14]. The GRL technique computes the error coefficients from measurements made on an empty fixture and a measurement made on a metal plate of known thickness. Time-domain gating was employed. This technique requires fewer standards than the existing thru-reflect-line (TRL) and thru-reflect-match (TRM) calibration techniques. Permittivity calculated from measurements, calibrated using this technique, made on a material sample appear to be superior to results using the TRL and TRM calibration technique as reported in [14].

The dynamic range of the free-space setup could be obtained from the measurement of transmission coefficient of a piece of metal plate after GRL calibration, which is supposed to isolate transmitter from receiver. The dynamic range of the whole system after GRL calibration is 50 dB from 4 to 8 GHz and 70 dB from 8 to 20 GHz. Thickness of the composite sheet under measurement is about 0.85 mm.

From the measured complex transmission coefficients *T*, complex effective permittivity $\varepsilon$ can be obtained, with the assumption that the layer is nonmagnetic, by solving the following equation with Agilent material software 85071E:

$$T = \frac{P\left(1-\Gamma^2\right)}{1-\Gamma^2 P^2} \tag{1}$$

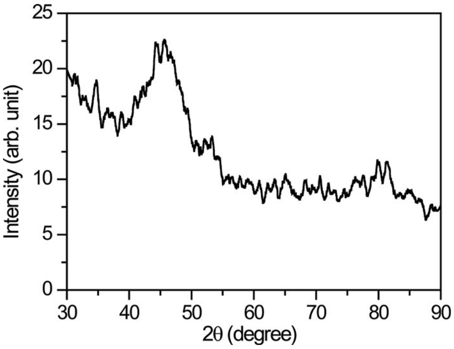

Fig. 4. XRD spectrum of microwires.

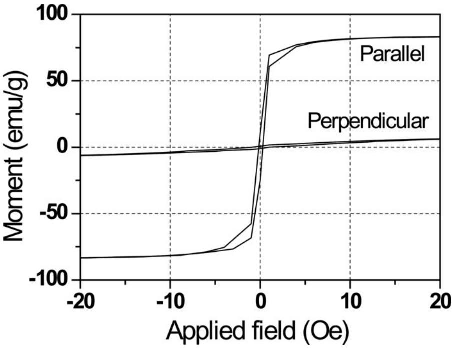

Fig. 5. Hysteresis loop of microwires.

where $\Gamma = (\sqrt{\varepsilon}-1)/(\sqrt{\varepsilon}+1)$, $P = \exp(-2\pi \mathrm{i} t\sqrt{\varepsilon}/\lambda)$, $t$ is the thickness of the composite sheet, and $\lambda$ is the wavelength. SE of the samples in decibels can be calculated from the absolute value of transmission coefficient according to

$$\mathrm{SE} = |20\log_{10}(T)| \tag{2}$$

## IV. RESULTS AND DISCUSSION

XRD spectrum in Fig. 4 indicates that the CoFeNiSiB alloy prepared using the Taylor–Ulitovsky method has grain size of 1.3 nm. The main reason could be the quenching process during the preparation. Extremely high quenching speed could be realized with cooling water because the size of the microwires is only 12.5 $\mu$m. Although the precise cooling rate is hard to measure, it is well accepted that such small grain size can only be obtained when quenching speed is as fast as $10^5$–$10^6$ K/s. As shown in Fig. 5, the nanocrystalline microstructure results in a small coercivity ($H_C < 1$ Oe) and high saturation magnetization ($M_S \sim 80\,\mathrm{emu/g}$), as well as high intrinsic static permeability along axial direction up to 1000 [9]. Static- and high-frequency permeability of the microwires with different alignments has already been investigated with impedance and coaxial measurement in our previous work [9]. Magnetic properties of the composites are not discussed in this paper.

Effective permittivity of the silicone composites loaded with randomly distributed microwires from 0.1% to 1% mass concentration and regularly distributed microwires are plotted in Fig. 6. Since the concentration of the mcirowires is too low, effective permeability of the composite is close to 1. Therefore, only

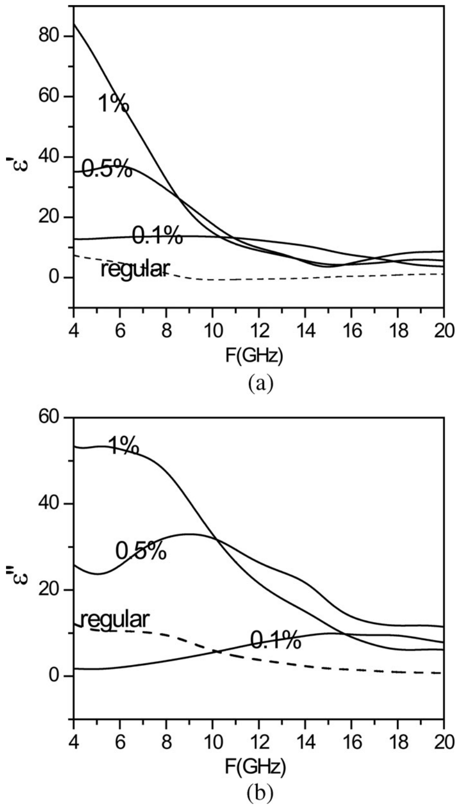

Fig. 6. Effective permittivity of the microwire composites. (a) Real part. (b) Imaginary part.

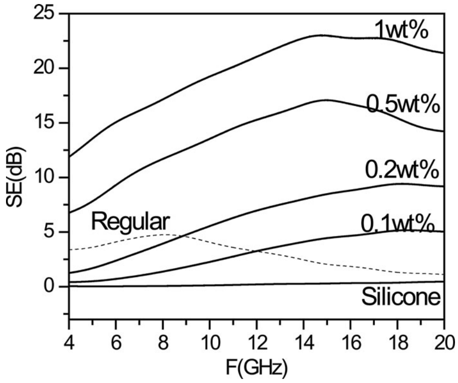

Fig. 7. SE of microwire composites.

effective permittivity is presented. A smoothly resonant behavior could be observed in all samples. This could be addressed to two possible effects: 1) the nonperfectly uniform distribution of filler within the matrix; 2) the typical resonance behavior of electrically long fibers embedded in a polymeric matrix, as described in [15]. It is noted from experiments that such smooth-resonance frequency shifts from 15.2 GHz at 0.1%, to 9.0 GHz at 0.5%, and 5.2 GHz at 1%. Theoretically, the resonance frequency $f_{\mathrm{res}}$ of a composite sheet of 5-mm conductive fibers embedded inside silicone matrix with permittivity of 3 is about 17.3 GHz. It is expected that $f_{\mathrm{res}}$ would be shifted down if the loading effect of the Pyrex glass coating is taken into account, because the typical permittivity of Pyrex glass (4–10) is larger than that of silicone (∼3) sheet according to the free-space measurement. So, $f_{\mathrm{res}}$ of composite with low concentration are more or less determined by the size of individual fibers.

When fibers are overlapped with each other, the fibers form fiber clusters and the resonance frequency will be brought down to lower value no matter whether they are electrically connected or isolated, which is called cluster effect [15]. Cluster effect of long conductive fibers with insulation coating could be able to explain the observed change of the smooth resonance plotted in Fig. 6. Two resonance peaks at 14 and 9 GHz could be observed in the composite with 0.5% fibers. It means that most fibers are either separated or form two-fiber clusters. For the sample with 1% fibers, no resonance peak could be found at 15 GHz. Most of the fibers form fiber clusters and the clusters contain three or more pieces of fibers. Hence, only one resonance peak can be observed at low frequency (∼5.2 GHz). For sample of microwire with regular distribution, resonance phenomena could not be found since length of the microwire is much longer than wavelength. Similar structure of microwire with 3-mm spacing was investigated by Reynet *et al.* [16], and similar results were obtained by us. The magnitude of the effective permittivity of the regular sample is close to that of the 0.1% sample, but they possessed different type of resonances. Effective permittivity of the samples decreases significantly when frequency is above 10 GHz. Dielectric loss tangent of regular sample is more than one over the whole frequency range. Such effective permittivity of regular distribution can only be found when incident wave has single polarization. The effective permittivity of the other direction is close to that of silicone matrix according to free-space measurement.

Microwire composite sheets with a thickness of 0.85 mm exhibit satisfactory shielding performance considering that concentration of the microwire is below 1%. SE of the 1% composite is better than 20 dB at frequency above 11 GHz. SE of the 0.5% sample could be above 17 dB at 15 GHz. For regular arranged microwire composites, SE decreases rapidly with frequency. High-frequency performance is much worse than that at low frequency. Our shortcut microwires overcome this problem through the resonance phenomena of the individual fibers or clusters. Hence, they have better high-frequency SE than the regular sample.

## V. CONCLUSION

Optically transparent composite sheets were fabricated with glass-coated ferromagnetic microwires and silicone matrix. Effective permittivity of the composite and SE of 20 cm × 20 cm sheets were measured with free-space setup. The smooth-resonance peak of imaginary permittivity of sample with randomly distributed short fibers could be explained by the length of the individual fibers and fiber clusters, even if some effect could be addressed to the nonperfectly uniform distribution of the filler within the matrix. Due to their high real and imaginary permittivity, SE of a microwire composite sheet with thickness of 0.85 mm could be up to 23 dB.

As compared with the composites with long and aligned microwires, short microwire composites have better effective permittivity, lower dielectric loss, and better shield performance at high frequencies. Besides, these microwire composites may also be used as broadband absorbing material due to their high and dispersive dielectric permittivity.

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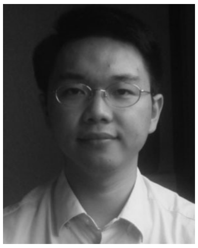

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