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Abstract — Electrical properties of nano-composite materials are extracted to investigate the possibility to engineer novel material for microwave applications. A measurement setup is developed to characterize material in a powder form. The developed measurement technique is applied on nano-particles of alumina, carbon nanotubes (CNTs), and composite mixture of carbon nanotubes and alumina. The effect of packing density on dielectric constant and loss tangent is thoroughly characterized experimentally. The obtained results show that the real part of effective permittivity may be considerably enhanced by increasing the percentage of conducting nano-particles. In addition, it is possible to decrease the loss in a material by mixing low-loss dielectric nano-particles powder in a lossy material.

Index terms — Alumina nano-particles, carbon nanotubes, composite material, microwave characterization, nanotechnology, percolation, permittivity measurements.

I. INTRODUCTION

Materials in pulverized form are challenging to characterize due to the density-dependence of electrical properties and the presence of air gap between particles. However, it is a decisive step to understand and design novel materials for future radio frequency (RF) devices. The electrical characterization of composite material is particularly interesting for their new electrical properties [1]-[2]. Nelson [3] has described different models to estimate the complex permittivity of bulk material from its pulverized form. However, those models fail in the case of nano-particles as explained in [4] where it is observed the enhancement of the real part of the permittivity of composite nano-material. Also in [5], it is reported at low frequencies in the range of few MHz dramatic values of complex permittivity for carbon nanotube networks where percolation theory [6] is used to interpret the reason for high values for both real and imaginary parts of complex permittivity.

The objective of this work is to explore changing in a controlled manner the complex permittivity of nano-particles of alumina by mixing with carbon nanotubes. For this purpose, the complex effective permittivity of pure alumina nano-particles is obtained. Then, carbon nanotubes in a dry-powder form as furnished by the manufacturer are characterized. Finally, we show that by mixing alumina and CNT in a controlled approach, it is possible to synthesize a novel nano-composite material with interesting electrical properties which could have appealing RF applications.

II. DESCRIPTION OF TEST STRUCTURE

The measurement setup used in this work for material characterization consists mainly of a hollow circular waveguide shorted at one end to hold the pulverized material under test (MUT). This hollow cylinder corresponds to region IV shown in Fig. 1 (a) and it is connected to a 50-Ω air-filled coaxial transmission line that corresponds to region I through regions II and III which are air-filled coaxial transitions. The technique of complex permittivity extraction involves an iterative optimized gradient method where the simulated reflection coefficient is compared to the one obtained from microwave measurements using a performance network analyzer (PNA). In this inverse optimization problem, the effective complex permittivity (\(\varepsilon_{\text{eff}} = \varepsilon_{\text{eff}}' - j\varepsilon_{\text{eff}}''\)) of the material under test is the unknown optimization variable. The search for complex permittivity stops when the absolute difference between the measured and simulated reflection coefficients is less than \(10^{-6}\)[19]. The simulation is based on full-wave modeling where coaxial and circular discontinuities are modeled using mode matching technique (MMT) [7]. Each discontinuity is characterized by its generalized scattering matrix (GSM) block. The different blocks of GSMS are connected in cascaded as shown in Fig. 1 (b) through transmission lines that represent the actual lengths of different regions. The final structure is modeled as a one-port network characterized by its reflection coefficient \(S_{11}\). It is noted that full-wave analysis based on MMT accurately models the discontinuities in cascade encountered by an incident electromagnetic wave as it involves all propagating and evanescent modes of each region depicted in Fig. 1 (a).
the frequency range from 10 MHz to 50 GHz using a single test setup [7]. The fabrication tolerance of the micro-machined test setup as verified by optical methods is less than 10 μm.

III. RESULTS AND DISCUSSIONS

The microwave measurements are carried out for pure alumina powder, carbon nanotubes, and a mixture of CNTs and alumina. The alumina used in this work is supplied by South Bay Technology, Inc. The nano particles of alumina have a diameter of 50 nm. The CNTs are provided by Bucky USA (product number BU-203) and they have a purity > 90 wt%, ash < 1.5 wt%, diameter 1 nm to 2 nm, and length 5 μm to 30 μm. For each material, nano-particles are weighted then dropped directly into the hollow-cylinder (region IV) holder. MUT is packed in the holder by exercising manual press through a plunger and a plunger support as shown in Fig. 2 (a) and (b), respectively, to progressively increase the density inside the holder shown in Fig. 2 (d). The volume of cavity $V$ is determined using optical measurements and the weight $M$ of MUT is obtained using analytical balance with ±0.01mg precision. The packing density is computed using the following relation: $\rho = \frac{M}{V}$.

A. Nano-Particles of Alumina

Dry powder of only nano-particles of alumina is used as furnished by the manufacturer. The average size of alumina particles is 50 nm. Fig. 3 shows the real and imaginary parts of the complex effective permittivity of pure alumina versus frequency at different packing densities.

Fig. 4 presents the variation of complex effective permittivity of alumina versus packing density and volume fraction at a frequency of 3 GHz. Volume fraction is defined as the ratio of the actual volume of nano particles to the total volume of container. In this case, alumina is weighed and the volume is obtained from $V_{act} = \frac{M}{\rho}$ where $\rho = 3.9$ g/cm$^3$ for alumina. The volume of holder cavity is 0.7854 cm$^3$. The linearly extrapolated results shown in Fig. 4 suggest that if a packing density equal to the bulk density of alumina is reached then the bulk permittivity of alumina is obtained. This linear variation of complex permittivity versus packing density is different from those models initially proposed in [3] for particles with sizes between 50-100 μm and discussed in [4] to extract bulk permittivity. The reason that initial models introduced in [3] fails for nano-particles is attributed to the reduction of air gaps between particles synthesizing a better homogeneous material as illustrated by the cartoon in Fig. 5 where particles are assumed to be spherical in shape. In other words, solid spheres corresponding to the alumina particles with larger radii leads to bigger voids between the particles which is equivalent to an air-alumina mixture and the effective permittivity of the mixed material is dominated by the air permittivity. As the radii of alumina particles decrease, voids
between the solid spherical particles are reduced. As the size of interstices becomes smaller than the wavelength of the electromagnetic waves propagating in the material the alumina nano-particles can be considered quite a homogenous medium.

The size of air interstices between alumina nano-particles decreases, their number has significantly increased. It is reported in [9] that the losses are less sensitive for granular particles with size greater than 3-4 μm in a fully dense material. However, for this case study, the loss dependence is strongly influenced by the porosity of the alumina nano-particles. This explains why the extracted imaginary part of the complex effective permittivity shown in Fig. 4 is higher than the one obtained in [9] for sintered alumina.

![Fig. 5: Schematic of alumina particles explaining the dependence of material electrical properties on the size reduction of particles from 50-100μm (left-hand side) to 50nm (right-hand side). Dimensions are not to scale.](image)

It should be noted that the packing density of alumina in the holder is progressively increased. Hence, the ratio of air to alumina is decreasing as the packing density is increased. For the particular scenario where packing density is 0, the holder is entirely empty, i.e., filled with air and the extracted permittivity corresponds to the case of air as shown in [19].

**B. Carbon Nanotube Networks**

CNTs are tested as supplied by manufacturer in their dry-powder form. Fig. 6 shows the complex effective permittivity at different packing densities.

![Fig. 6: Variation of the complex permittivity of carbon nanotube networks in a dry-powder form at different packing densities when the structure shown in the inset is filled with MUT. Different markers are assigned for each density. The solid lines represent the real part \( \varepsilon'_r \) of the permittivity while the dashed lines correspond to the imaginary part \( \varepsilon''_r \). Both real and imaginary parts have the same scale.](image)
dramatic value of real and imaginary parts of complex permittivity obtained at lowest frequency and highest density are in agreement with those large values reported in [5], [12] and [17].

The effective complex permittivity is plotted in Fig. 7 versus packing density. The imaginary part of the permittivity \( \varepsilon'' \) is related to the conductivity of the CNTs: \( \varepsilon'' = \frac{\sigma}{\omega \varepsilon_0} \) where \( \omega \) is the angular frequency and \( \varepsilon_0 = 8.85 \times 10^{-12} \, (\text{F/m}) \) is the vacuum permittivity. In the inset of Fig. 7, the real and imaginary part of the effective permittivity function of the density are plotted in log-log scale at 3 GHz to extract the relevant parameters of the percolation curves.

Above the percolation threshold \( p_c \), the real and imaginary parts of the effective permittivity of a conductor-insulator mixture can be expressed in terms of a power law relation as follows:

\[
\varepsilon', \varepsilon'' \propto (p - p_c)^t \quad \text{for} \quad p > p_c
\]

where \( p \) is the occupation probability and \( t \) is the critical exponent. It should be noted that the CNT networks include metallic nanotubes, semiconducting nanotubes, and air voids. Hence, the variable packing density is adopted in this work to describe the percolation behavior instead of the volume/weight fraction. The critical exponent \( t \) is usually between 1.6 and 2 in a three dimensions percolation networks. However, experiments show that its value varies from 1.3 to 3.1 [13]. In Fig. 7, the percolation threshold \( p_c \), corresponding to the packing density of 0.16 g/cm\(^3\) represents the onset of material changing behavior from dielectric to conductive. For the studied CNTs, the critical exponent obtained by the linear regression fitting curve of the imaginary part of the effective permittivity shown in the inset of Fig. 7 is 1.8 at 3 GHz which agree with the percolation data reported in the literature. The region below percolation threshold where the dielectric constant increases rapidly has been studied experimentally and theoretically in [14]. Below percolation threshold, it is observed that the material behaves as an insulator a large

Fig. 7: Variation of the real (dot) and imaginary (cross) parts of the complex effective permittivity of carbon nanotube networks versus density at 3 GHz. The inset presents the log-log plots of the real and imaginary part of the complex effective permittivity functions of the occupation probability. The dashed lines in the inset are the means values fitting curves based on equation (1).

In this work, we study the nano-material characteristics above its percolation threshold where it behaves as a conductor. Thus, a saturation followed by decreasing of the real part of the permittivity versus packing density is observed while the imaginary part continuously increases as shown in Fig. 7. Applying (1) to the fitting curve of the real part of the permittivity shown in the inset of Fig. 7, gives a negative critical exponent (-0.15) due to the decrease of the dielectric constant. The fact that the dielectric constant decreases above percolation threshold with the increase of packing density is because the material under test becomes more conducting due to the increasing number of metallic nanotubes. Ultimately, the real part of the permittivity should theoretically reach 1 as for a metallic material.

It is noted that the CNT networks as produced by manufacturer consist of a 1:2 ratio where 1/3 of metallic nanotubes is mixed with 2/3 of semiconducting nanotubes [15]. At low frequencies, the interaction between metallic and semiconducting nanotubes enhances the real part of complex effective permittivity. In [4], the experimental measurements applied to a mixture of nano-particles of alumina and micro-particles of copper show the contribution of packing density and the composition of a mixture of metallic-dielectric nano particles to the large values of complex permittivity. Moreover, studies in [1] and [16] suggest that the nonlinear behavior of permittivity can be enhanced by changing the aspect ratio of mixed nano-particles. At low frequencies, the interaction between metallic and semiconducting nanotubes enhances the real part of complex effective permittivity. In [4], the experimental measurements applied to a mixture of nano-particles of alumina and micro-particles of copper show the contribution of packing density and the composition of a mixture of metallic-dielectric nano particles to high values of complex permittivity. Two-physical mechanisms may explain this permittivity enhancement [5] and [18]. First, electrical field creates a surface charge polarization on the interface between metallic and dielectric particles which yields an increase in capacitance. Second, dipole polarization contributes to global permittivity when the frequency of applied electrical field is lower than the relaxation frequency of metallic particles.

In Fig. 8, the locus in the complex plane of the relative complex permittivity divided by bulk density for carbon nanotube networks can be used to predict the behavior of the material.
C. **Mixture of Alumina and Carbon Nanotubes**

This section is dedicated to the extraction of the complex permittivity of CNT-based composite materials. The CNT-based composite material is realized by mixing 1g of alumina with 0.2g of CNT. Transmission electron microscopy (TEM) of prepared mixture is shown in Fig. 9.

Another procedure used to characterize the mixture is the Energy-dispersive X-ray spectroscopy (EDX) shown in the inset of Fig. 9. The EDX where three peaks can be distinguished is representative of the mixture sample realized at different positions in the sample. The first peak indicates the presence of carbon due to CNTs as well as the carbon grid used to deposit the samples explaining the high magnitude compared to other components. The second and third peaks indicate the presence of oxygen and aluminum due to alumina particles (Al₂O₃).

Based on our previous studies [5], [17], [19] as well as the work reported here, the extracted complex permittivity of CNT networks is significantly large at low frequencies as shown in Fig. 6 and drops by several orders of magnitude at higher frequencies. This trend is observed independent of the packing density. At higher frequencies, both real and imaginary parts of the effective permittivity converge to asymptotic values corresponding to bulk material. As we anticipate that the main effect due to the addition of CNTs in alumina medium occurs at low frequencies, we have limited the maximum measurement frequency to 3 GHz.

The complex permittivity of the composite mixture versus frequency from 10 MHz to 3 GHz at different packing densities is presented in Fig. 10. Fig. 11 shows the variation of the complex permittivity of a dry mixture of CNTs and alumina versus density at a frequency of 3 GHz. In this figure, the data obtained for pure alumina are also plotted to highlight the increase of dielectric constant due to the mixing with CNTs.
Moreover, CNTs and alumina are used as a reference to control the electrical properties of the medium [23] by introducing a small bias voltage across the composite material. This is another interesting application in tunable circuits. Moreover, CNTs composite materials were studied in [24] for electromagnetic interference (EMI) shielding to protect delicate electronic devices against external electromagnetic radiation. In the last decade, high-k gate dielectric appeared in semiconductor technology and progressively replaced silicon dioxide insulator layers to further miniaturize microelectronic components without sacrificing the performance of CMOS transistors at high frequency [25]. Our work shows that CNT-based composites may be a possible candidate as future high-k gate dielectric implemented in high-frequency silicon-based transistors.

Several research groups have demonstrated the RF applications in radio systems where carbon nanotubes detect an amplitude modulation (AM) signal in a functioning radio receiver as replacement of diode in current radio systems [26]-[27]. CNTs are also among the possible candidates to implement future high frequency transistors due to their quasi-ballistic electron transport and their high intrinsic cut-off frequencies (up to terahertz). The main challenge is to control the alignment and the deposition of CNTs to form a semiconducting channel between the drain and source. Several alignment techniques have been investigated such as droplet, dielectrophoresis, Langmuir-Blodgett, spin coating and chemical vapor deposition (CVD) methods [28]; however, fabrication of CNT-field effect transistor (CNT-FET) on a large scale integration still needs to be improved to be competitive compared to traditional silicon based FET.

V. CONCLUSIONS

A measurement approach is presented to extract the complex effective permittivity of nano-particles pulverized materials considering the effect of packing density. The technique is applied to nano-particles of pure alumina, carbon
nanotubes, and to a mixture of alumina and carbon nanotubes. For alumina, the linear dependence of complex effective permittivity on packing density gives an estimate of the permittivity of bulk material. The dramatic values of the real and imaginary part of the complex permittivity of CNTs at low frequencies are due to the interaction of metallic and dielectric nano-particles. The nonlinear behavior of the variation of the permittivity as a function of the packing density is experimentally demonstrated for a mixture of carbon nanotubes and alumina. The possibility to engineer CNT-based composites material with a high-dielectric constant and low loss has been shown. The compositions as well as the dispersion of the carbon nanotubes in a dielectric medium will be the key to engineer those new microwave composite materials.

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