

Infrared surface plasmon polariton on polyaniline-graphite composite

Monas Shahzad¹, Gautam Medhi¹, Doug Maukonen¹, Mehmet Yesiltas¹, R. E. Peale¹, Walter R. Buchwald², Justin Cleary³, Yi Liao⁴, Candace Alber⁴, Valentine K. Johns⁴, Rahul Hegishte⁴, Glen D. Boreman⁵

¹Department of Physics, University of Central, Florida, Orlando, FL 32816, USA

²Solid State Scientific Corporation, Hollis New Hampshire 03039, USA

³Sensor Directorate, Air Force Research Laboratory Wright Patterson, Air Force Base, Ohio, 45433, USA

⁴Department of Chemistry, University of Central Florida, Orlando FL 32816, USA

⁵Department of Physics and Optical Science, University of North Carolina at Charlotte, Charlotte NC 28223, USA

ABSTRACT

Conducting polymers are potentially useful materials in sensor applications. Polyaniline is one of the most promising of these materials due to high conductivity and plasma frequencies as high as the mid-infrared. The application of this material is still limited because of low conductivity. In this paper, we chemically prepared a composite of co-doped polyaniline with hydrochloric acid and MSA (methane sulfonic acid) in aqueous solution with both colloidal and nano-graphite. Solutions of the composite material were prepared in m-cresol and NMP (N-methyl-2-pyrrolidone), which are common organic solvents. This approach resulted in material with conductivity higher than either intrinsic polyaniline or graphite alone. The solution of the composite was spin coated on suitable substrates. The thicknesses of the films were measured using atomic force microscope (AFM). Fourier transform infrared spectra (FTIR) and micro-Raman spectra were collected to confirm the composition and determine the infrared thickness. Surface plasmon resonances for grating patterns of this composite material were calculated using experimentally determined infrared (IR) ellipsometry data. The goal is to identify a material which has potential application for surface plasmons resonance sensing with high sensitivity and selectivity in IR range.

Keywords: Infrared; Conducting polymers; Graphite; Surface plasmons.

1. INTRODUCTION

Surface electromagnetic waves occur at the interface between a dielectric and a conductor below its plasma frequency.¹ For these surface plasmon polariton (SPP) to be bound with sub-wavelength confinement, the real part of the permittivity ϵ' should generally be negative and the imaginary part ϵ'' small. Qualitatively similar bound surface waves can occur above the plasma frequency when $\epsilon' > 0$ if $\epsilon'' > \epsilon'$.² The principle commercial application of SPPs is in biosensors, where the change in the resonant coupling of light to SPPs gives information for identifying bio- molecules and quantifying their interactions. We hypothesize that potential sensitivity and selectivity advantages will accrue by operating SPP biosensors at wavelengths where biological analytes are strongly differentiated by their IR absorption spectra and where refractive indices are enhanced by dispersion^{2,3}. This requires materials with plasma frequencies in the mid-IR. This paper investigates conducting composites of the polymer polyaniline (PANI) and graphite. The conductivity of the composite can exceed that of either the graphite or polyaniline alone⁴, and hence may have mid-IR plasma frequency.

2. EXPERIMENTAL DETAILS

Polyaniline-graphite composite was synthesized by making 1 mol/L aqueous HCl solution (pH between 0 and 2). Ammonium persulfate was used as oxidant with an oxidant/aniline (monomer) molar ratio ≤ 1.15 . The colloidal and nano-graphite with average particle size less than 0.5 microns were added according to the amount desired in the final product⁴⁻⁶. The aniline (monomer) concentration was 0.1 mol/L. The solution temperature was 0°C in order to limit secondary reactions. The duration of reaction was 2 h. Aqueous ammonium persulfate solution was added slowly drop by drop to the aniline-graphite/HCl solution. The mixture was stirred continuously during the whole reaction. The formed precipitate was removed by filtration and washed repeatedly with HCl acid solution and dried for 48 h. It was secondarily doped with 1 M aqueous solution of MSA (methane sulfonic acid). The obtained product was washed and dried under vacuum for 48 h. Resistivity of pressed pellet of the composite material was measured using four contact method to be in the range $\rho = 0.005 \Omega\text{-cm}$. The highest conductivity measured was 200 S/cm for 90/10 mass ratio of pani-graphite composite. The conductivity of the composite is higher than the individual constituents of the composite, 154 S/cm and 10 S/cm for pristine graphite powder and polyaniline, respectively. By changing the mass ratio of the two components, an increase in electrical conductivity was detected which is due to intercalation of polyaniline chain inside graphite particles for facilitating the charge transfer in the composites⁶.

Polyaniline-graphite solutions of 5 and 10 wt % were prepared with solvent m-cresol and NMP. We spin-cast the polyaniline-graphite solution at 3000 and 2500 rpm for 0.5 and 1 min, respectively, to obtain different film thickness in different samples. DC conductivities were measured using four contact methods. The conductivities of the composite thin film in organic solvent turned less than the conductivities in powdered form.

To measure the infrared penetration depth, films of different thickness were deposited on un-doped double-side polished silicon. Transmission measurements were made using a Fourier spectrometer. Mechanical thickness was measured using atomic force microscopy near a scratch in the film. These measurements allowed us to determine the thickness needed in the subsequent ellipsometry measurements to avoid contributions from the substrate. Complex permittivity of pani-graphite optically thick film in m-cresol and NMP were determined using a J.A. Woollam IR-VASE in wavelength range 1-40 micron.

3. THEORETICAL CONSIDERATIONS

The raw ellipsometry output of thin film of composite material was used to calculate complex permittivity $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ data based on standard Fresnel equations assuming an optically thick film⁷.

The raw ellipsometry output is $\tan\psi$ which is the real amplitude of the complex reflectance ratio of p- to s-polarized light, and Δ , the phase shift between the two reflected polarizations. From these wavelength dependent measurements the complex permittivity was determined for a given angle of incidence θ using Eq. (1) and (2).

$$\epsilon' = \sin^2(\theta) \left[1 + \frac{\tan^2(\theta)(\cos^2(2\psi) - \sin^2(\Delta)\sin^2(2\psi))}{(1 + \sin(2\psi)\cos(\Delta))^2} \right] \quad (1)$$

$$\epsilon'' = \sin^2(\theta) \left[1 + \frac{\sin^2(\theta)\tan^2(\theta)\sin(4\psi)\sin(\Delta)}{(1 + \sin(2\psi)\cos(\Delta))^2} \right] \quad (2)$$

The IR penetration depth into the composite material, δ , was determined using

$$\delta = \frac{c}{\omega} \text{Im}(\sqrt{\varepsilon}) \quad (3)$$

Gratings serve as couplers between photons and SPPs⁸. They function by shifting the incident photon wave vector by integer multiples, m , of $2\pi/p$, where p is the grating period. The wave vector shift compensates for the inherent momentum mismatch between light and SPPs. Grating couplers allow multiple resonant SPP excitations to occur due to the multiple units of grating momentum that may be added to the incident wave vector. The coupling condition between an EM wave that is incident from the dielectric at an angle θ onto a grating and a SPP is

$$\eta_d \sin(\theta) + m \frac{\lambda}{p} = \pm \frac{c}{\omega} \text{Re}[k_{spp}] \quad (4)$$

Where m is an integer of either sign. The refractive index η_d of the dielectric above the grating is important in biosensing applications, since it changes and causes the resonance angles to shift due to surface binding of the analyte molecules.

Calculation of angular reflection spectra was performed using the theory of Hessel and Oliner^{8, 9} with a simplified model of the grating as a sinusoidal modulated surface impedance with amplitude M . The average surface impedance relative to that of free space (337Ω) is

$$\xi = -i \left(|\varepsilon'|^2 + \varepsilon''^2 \right)^{-1/4} \left\{ \cos\left(\frac{\phi}{2}\right) + i \sin\left(\frac{\phi}{2}\right) \right\} \quad (5)$$

where ε' and ε'' are the real and imaginary parts of the conductor permittivity, respectively, and $\phi = \tan^{-1}(\varepsilon''/\varepsilon')$. A coefficient D_n is defined as

$$D_n = \frac{2}{M} \left[1 + \frac{1}{\xi} \sqrt{1 - \left(\sin \theta + \frac{n\lambda}{p\eta_d} \right)^2} \right] \quad (6)$$

where n is an integer and modulation parameter M is a function of grating permittivity, amplitude, and wavelength. For the calculations of this work, M is varied to fit measured data or to optimize the theoretical resonance line shape and strength. Finally, the specular reflectance of the grating is calculated by

$$R \approx \left| 1 - \frac{4 \cos \theta}{M \xi (D_0 - D_1^{-1} - D_{-1}^{-1})} \right|^2 \quad (7)$$

The sinusoidal surface impedance approximation and the neglect of higher order D_n term in Eq. (6) gives a calculated angular reflectance spectra in which only the $m=1$ resonance appears.

4. RESULTS

Table 1. Optical parameters Polyaniline-Graphite composites. Permittivities and complex surface impedances are given at 9.25 micron wavelength.

Composite materials	ρ (Ω -cm)	ε'	ε''	ξ [Eq.(5)]
PANI/CGP in m-cresol	0.056	3.1343	4.1371	0.3948 -i0.1954
PANI/CGP in NMP	0.166	1.8712	3.1570	0.4535 -i0.2584
PANI/NGP in m-cresol	0.337	3.5557	3.2682	0.4240 -i0.1652

4.1 Polyaniline/Graphite Composite

Fig. 1 present micro-Raman spectra of the polyaniline emeraldine salt (ES) and colloidal, nano-graphite polyaniline composite. The major peaks are labeled with their frequencies. The Raman spectra of ES polyaniline shows the vibrational modes at 800 cm^{-1} , 1180 cm^{-1} , and $1300\text{-}1600\text{ cm}^{-1}$. For both composite materials, the vibrational modes of PANI were detected at the same position and were not affected by the presence of graphite. Two vibrational modes around 1500 cm^{-1} and 2700 cm^{-1} are the first and second order Raman spectrum of graphite. These peaks match the published data⁴ as shown in figure 2.

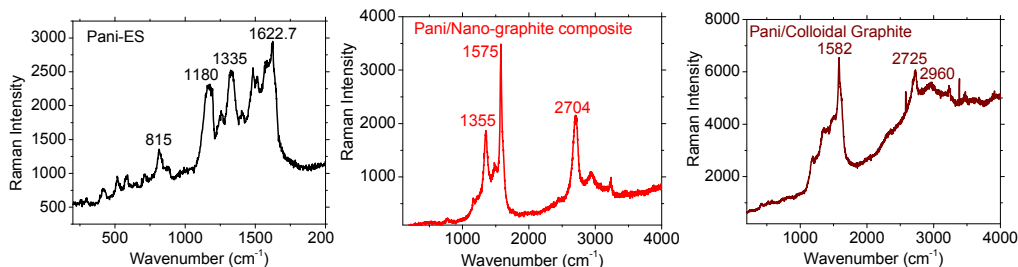


Fig. 1 (left) Micro-Raman spectra of Pani/Colloidal graphite composite (centre) and Pani/ Nano-graphite composite (right) Polyaniline emeraldine salt (Pani-ES).

Fig.2 shows the published data⁴ of micro Raman spectra of polyaniline, pristine graphite powder and the composite of PANI-Graphite. The shift in the vibrational mode of graphite for peak 1586 cm^{-1} in the new composite material shows the strong interaction of graphite with polyaniline. This Raman spectra changes in the composite can be explained because of the shift of Fermi level of graphite due to interaction with polyaniline which has affected the electrical properties of the composite.¹⁰

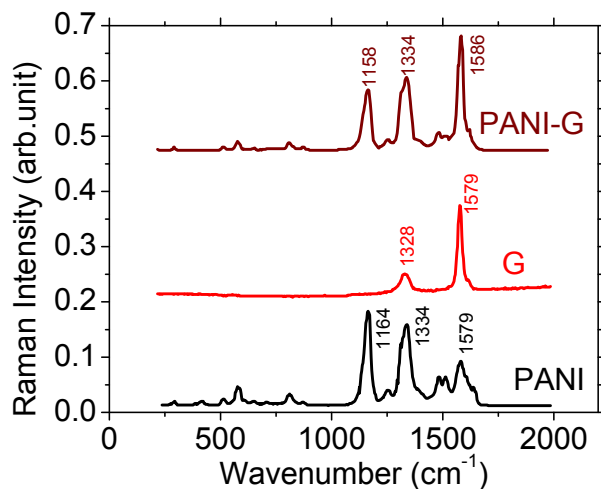


Fig. 2 Micro-Raman spectra (published data) of Polyaniline, Graphite and the composite material

Fig. 3 (left) presents the raw ellipsometry spectra (ψ , Δ) in the wavelength range 1-40 micron at incidence angle of 75° for each composite prepared. These data are used to calculate the permittivity using Eq. (1) and (2). Fig. 3 (right) presents permittivity spectra of polyaniline/colloidal graphite thin film in organic solvent m-cresol. The real part of the permittivity never goes negative in this wavenumber range. The imaginary part of the permittivity always exceeds the real part. These conditions in principle still permit the appearance of a bound surface wave that is qualitatively similar to an SPP².

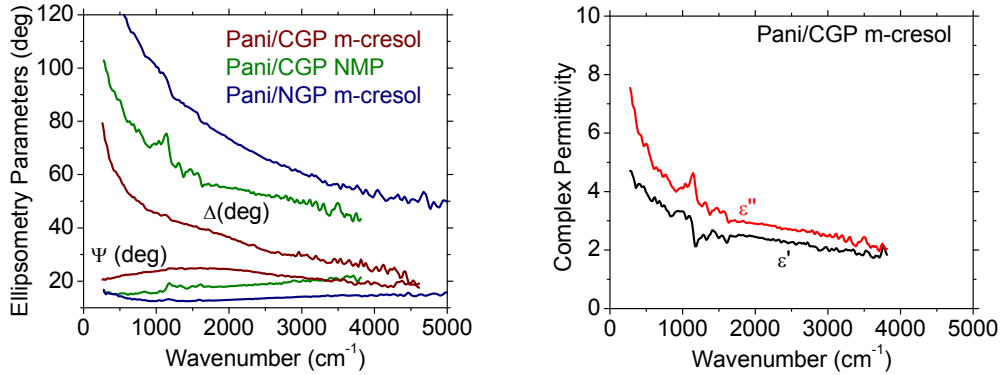


Fig. 3 (left) Raw ellipsometry data. (right) Real and imaginary parts of permittivity of Polyaniline/Colloidal graphite (CGP) in m-cresol, from ellipsometry.

Fig. 4 presents a plot of the complex permittivity for the colloidal graphite (CGP) and nano graphite (NGP) composites with polyaniline in NMP and m-cresol. For the composite material Pani/CGP in NMP the imaginary part of the permittivity exceeds the real part. In Pani/NGP with m-cresol, both real and imaginary parts are similar throughout the spectrum. In both cases the ϵ' values are positive, though bound surface waves can still occur² when $\epsilon'' > \epsilon'$. We note that for all samples the imaginary part of the permittivity follows the expected behavior, i.e. it is positive and it trends like $1/\text{frequency}$, as expected for conductors. The behavior of the real part is more difficult to explain, since for a conductor it should become negative at some point in going toward low frequencies and then continue heading toward larger negative values. None of the ϵ' plots behave this way.

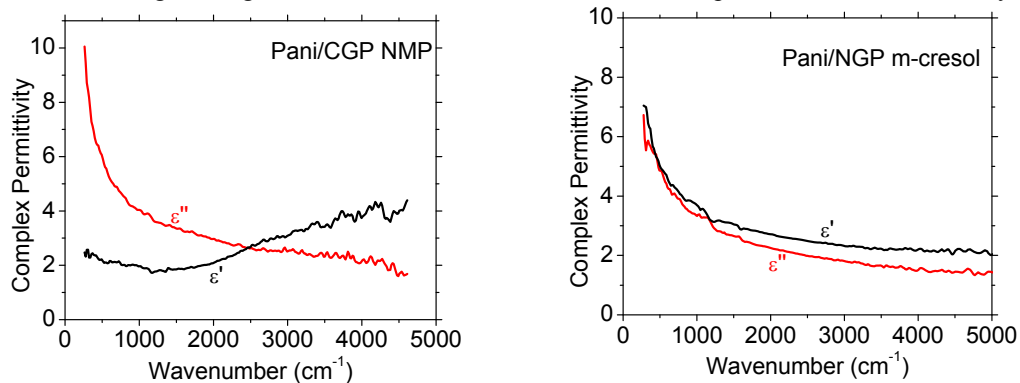


Fig. 4 (left) Real and imaginary part of permittivity for polyaniline/Graphite composites for colloidal graphite (CGP) and nano-structured graphite (NGP) and nano-graphite from ellipsometry data.

The IR-field penetration depth into the conductor, δ , was determined using equation (3) to be 5 microns at 9.25 micron wavelength. This value was qualitatively confirmed by FTIR spectrum of a spin-cast film of composite material on double polished silicon. The spectrum in the range 2-10 micron wavelength is presented in Figure 5 (left). The transmittance is almost zero for 5-micron-thick film across the mid infrared which is in agreement with expected IR penetration depth.

Expected resonance angles and the angular spectra are calculated using the ϵ' and ϵ'' values according to Eq. (7), assuming a 20 micron period grating and using $M = 1$. Figure 5 (right) presents the calculated reflectance spectra of SPPs for composite material thin film in two different organic solvent. For good conductors, we expect to see a sharp deep resonant decrease at a particular angle, usually asymmetric and with a cusp on one side. When the amplitude of the grating is too high, the imaginary part of the permittivity too large, or the real part too small or positive, the resonance is broadened, and only the cusp remains sharp. We see such a cusp in the calculated reflectance spectrum for our material's permittivity at around 32 degree.

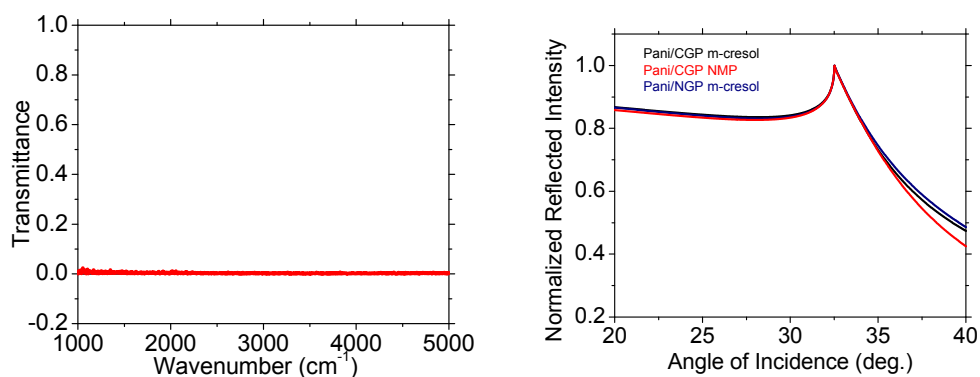


Fig. 5. (left) FTIR Spectrum of 5 μm thick Polyaniline/CGP Film. (right) Calculated angular reflectance spectra for 20 micron period gratings and p-polarized 9.25 micron wavelength incident IR beam.

5. SUMMARY

IR permittivity data was presented for spin-coated composites of conducting polymer and graphite. Results show small positive values across the spectrum for both real and the (generally larger) imaginary parts. Under such conditions bound surface waves are possible. Calculations show possibility of surface-wave excitation resonances for gratings formed from these materials. These resonances should be sensitive to changes in the refractive index above their surfaces and hence should have potential to be used as for IR sensor applications.

Acknowledgment

This work was supported by AFOSR grant number FA 95501010030, Gernot Pomrenke, Program Manager

REFERENCES

- [1] Maier S. A *Plasmonics: Fundamentals and Applications* (Springer, 2007).
- [2] Cleary J. W., Peale R. E. "Infrared surface polariton on antimony", *Optics Express*, 20, 2693 (2012).
- [3] Cleary J.W., Medhi G., Peale R.E., Buchwald W. R., Edwards O., and Oladeji I., "Infrared Surface Plasmon Resonance Biosensor", *Proc. SPIE 7673*, 5 (2010).
- [4] Shawn B.E., Tito V, "Graphite/Polyaniline (GP) Composites: synthesis and characterization," *Carbon* 43, 2983 (2005).
- [5] Syed A. A., Dinesan M. K., "Polyaniline a novel polymeric material," *Talanta* 38, 815 (1991).
- [6] Bourdo S., Li Z.A., Alexandru S.B., Watanbe F., Tito V., and Paval I., "Structural, Electrical, and Thermal Behavior of Graphite-Polyaniline Composites with Increased Crystallinity", *Adv. Funct. Mater.*, 18, 432 (2008).
- [7] Tompkins H. G, *A use's guide to ellipsometry* (Academic, San Diego, 1993).
- [8] Cleary J.W., Medhi G., Peale R.E., and Buchwald W.R., "Long-wave infrared surface plasmon grating coupler", *Appl. Optics* 49, 3102 (2010).
- [9] Hessel A. and Oliner A.A., "A new theory of Wood's anomalies on optical gratings," *Appl. Opt.* 4, 1275 (1965).
- [10] Fischer E. J, "Graphite intercalation compounds :Electronic properties and their correlation with chemistry", *Physica B+C*, 99, 383, (1980).