Tunable silicon carbide – polyethylene nanocomposites: correlation between mass ratio and surface phonon-polariton resonance properties.

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Abstract  Towards developing passive tuning elements, we demonstrate that controllable thermal conductivity and heat transfer at the nanoscale can be achieved using mass ratio preparations of silicon carbide (SiC) nanoparticle based polyethylene (PE) nanocomposites. By use of titration and gradual increases in temperature during mixing, we observe in the resulting nanocomposites, correlations between surface phonon—polariton activity and mass ratio. We present results for mass ratios (PE:SiC) equal to 1:1, 5:1, 10:1, 15:1, and 20:1. For SiC, surface phonon-polariton activity is observed (in the range, 763 to 996 cm⁻¹). We estimate using a kinetics study that equivalent comparison between samples with different mass ratio is accomplished after 5 days of drying. Changes in refraction index present unintended changes in absorbance due to the high refraction index of SiC and carbon black. Our initial results highlights that the use of mass ratio in nanocomposites establishes a parameter for passive tuning of the effective thermal conductivity.

1 Introduction

Materials engineered for heat transfer applications can be structured at the nanoscale to raise the efficiency of infra-red (IR) devices and applications. Surface phonon-polaritons are excitations that can be stimulated using infra-red light on polar crystals to control thermal conductivity at the nanoparticle scale [1, 2]. In addition to applications in optical sensing, mid-IR surface phonon-polaritons uses include near-field superlensing, surface wave particle acceleration, and efficient thermal emission [2]. By regulating thermal transmission, future semiconducting devices may better distribute heat, in a fashion that protects sensitive components. Tunable infra-red excitation and/or thermal management at the nanoscale support the concept of a self-actuated interface for thermal transport. Direct tuning of a material’s response is not always possible so passive tunable methods are sought to manage heat transfer in a non-destructive fashion.

In this paper, we present a passive tuning element for heat transfer using nanocomposites of silicon carbide (SiC) and polyethylene (PE) for different mass ratios as illustrated in Figure 1 when measured by Fourier Transform Infra-Red Spectroscopy with an attenuated total reflection attachment (FTIR-ATR). Polyethylene, does not support surface phonon-polariton coupling (nor does it have absorptive peaks in the SiC phonon-polariton range, 763 – 996 cm⁻¹), and acts as a nanoparticle spacer. Both SiC and silicon dioxide (SiO₂) exhibit surface phonon-polariton
resonances for both wafers, and nanoparticles as discussed in this work [1-3]. SiO$_2$ is a common material used in microfabrication and materials processing. SiC shows promise as a metamaterial and similarly is a polar material with a lattice resonance in the thermal infrared causing a wavelength interval with a negative dielectric function [4]. In this wavelength interval, SiC can support surface waves [4]. Coupling of infrared (IR) light to surface phonon polaritons, is accomplished through the evanescent field established at the interface between the nanocomposite (with refraction index, $n_2$) and a high-index ($n_1$) zinc selenide (ZnSe) prism as shown in Figure 1. For maximum coupling, transfer of all or most of the incident radiation into surface phonon polariton excitations is ideal. This “critical coupling” results in a vanishing reflectivity and the largest enhancement of the surface phonon polariton field over the incident laser field [2]. The aim for tunable elements is to manage sub-critical or lesser amounts of coupling.

In this paper, we highlight that mass ratio dependent nanocomposites show a correlation between inter-nanoparticle distances and surface phonon-polariton resonance. SiC nanoparticles in a polyethylene mixture are intended to be equally dispersed where inter-particle spacing can be adjusted by changing the mass ratio of nanoparticles to polyethylene. In Figure 2, the mixing model is illustrated a spherical nanoparticle sits in a cube with polyethylene and toluene components (before drying). The inter-nanoparticle distance, $x$, varies depending on the ratio of toluene and polyethylene present in the composite as seen in equations 1-4.

\[
x = \frac{D}{2} \left( \frac{4\pi V_{\text{TOT}}}{3\ V_{\text{SIC}}} \right)^{\frac{1}{3}} - 2
\]

\[
\frac{V_{\text{TOT}}}{V_{\text{SIC}}} = 1 + \frac{\alpha_T}{\beta_T} + \frac{\alpha_{\text{PE}}}{\beta_{\text{PE}}}
\]

\[
\alpha_T = \frac{M_{\text{toluene}}}{M_{\text{SiC}}} \ ; \ \alpha_{\text{PE}} = \frac{M_{\text{PE}}}{M_{\text{SiC}}}
\]

\[
\beta_T = \frac{q_{\text{toluene}}}{q_{\text{SiC}}} \ ; \ \beta_{\text{PE}} = \frac{q_{\text{PE}}}{q_{\text{SiC}}}
\]

The distance between nanoparticles, $x$, in Equation 1 can be estimated by the size or particle diameter, $D$, and the ratio of the total volume, $V_{\text{TOT}}$, to the nanoparticle volume, $V_{\text{SIC}}$. The volume ratio depends on the mass and density ratios $\alpha_i$ and $\beta_i$, respectively for $i = \text{T}$ (toluene) and ‘PE’ (polyethylene). Note that when $i = \text{SiC}$, $\alpha$ and $\beta$ identically equal 1.

Equation 3 shows us that as the mass of toluene decreases (i.e. evaporates), the smaller the total volume in Equation 2, which in turn decreases the inter-particle spacing as shown by ‘x’ in equation 1. Thus, with smaller inter-nanoparticle spacing we expect an increase in refraction index (related to the higher index nanoparticle).

Our synthesis approach uses mechanical mixing and thermal energy in order to disperse the
nanoparticles in the polyethylene polymer. With this approach, we aim to make a ‘ruler’ to see how nanoparticle spacing is affecting surface phonon-polariton resonance. Fourier Transform Infrared Spectroscopy (FTIR) with Attenuated Total Reflectance (ATR) as well as Scanning Electron Microscopy (SEM) was used to confirm optical phonon mode transmission and the spacing between nanoparticles.

2 Experimental details

A hotplate with a magnetic stirrer was first set to a temperature of 60°C. In a 100 mL beaker 0.5 grams of SiC powder [SiC beta, 97.5%, 45-55 nm CAS # 409-21-2 from Nanostructured and Amorphous Materials, Inc.] was used with PE:SiC = 5:1 and greater. A 1.0 g amount was used for the 1:1 recipe. A toluene volume equal to 3.5 times the volume of the measured polyethylene was added to the SiC. This set volume of toluene enhances good SiC mixing, and preserves a mixing reference where additional amounts of toluene are not supplied during the mixing steps. The SiC-toluene solution was sonicated with a plastic cover over top of the beaker to help prevent the toluene from evaporating too quickly for five minutes. After sonication, and to avoid sedimentation, a stirrer is placed inside with a low stir setting. A small fraction, 1/10, of the PE was then measured and added to the SiC - toluene solution and the temperature was manually increased 10°C. We cover the opening of the beaker with aluminum foil to prevent the toluene from evaporating too quickly. Every 10 minutes another batch, equal to the last batch (1/10 of the initial mass), of PE is added to the mixture as well as the temperature increase of another 10 degrees. 10 minutes after the last batch of PE is added, we leave the heat (set at 150°C) and stirrer on for an additional hour. After an hour, the heat is switched off and the aluminum foil is removed to let the forming nanocomposite dry. The stirrer continues until the composite solidifies around the stirrer bar. Using a drying kinetics study for the mass ratios 1:1, 5:1, 10:1, 15:1, and 20:1 polyethylene to silicon carbide, it was determined that at least 4 -5 days of drying time should be allotted before measurement.

For a given mass ratio, 10 samples are randomly selected and analyzed using the FTIR-ATR (Fourier Transform Infrared spectroscopy with Attenuated Total Reflectance) instrument to measure the nanocomposite’s surface phonon-polariton response. Samples are placed on the prism with a diameter that is roughly less than that of the force arm. Pressure was then slowly applied to sample until the pressure on the force arm is maxed out. 10 samples from each mass ratio are saved together. Both p- and s-polarized analyses are completed. A SEM analysis was also included to verify that proper mixing has been accomplished.

3 Results and Discussion

In this section, we assess our results using the FTIR-ATR spectra and surface phonon-polariton coupling as a guide. For each spectrum, along the vertical axis, ‘%T’ indicates the amount of reflectance or light reaching the detector after being internally reflected. Normally, %T would indicate transmittance, but in fact energy drawn across the interface, as in the case of surface phonon-polariton coupling, is considered to be absorbed or to result in low ‘%T’ values for a specified wavenumber. According to the Fresnel equations for reflection at an interface [5], based on Maxwell’s equations, the reflectance for p-polarized and s-polarized light are expressed in Equation 5 and 6 respectively.

\[
R_p = \frac{n_1 \cos \theta_1 - n_2 \cos \theta_1}{n_1 \cos \theta_1 + n_2 \cos \theta_1}^2 \quad (5)
\]

\[
R_s = \frac{n_1 \cos \theta_1 - n_2 \cos \theta_1}{n_1 \cos \theta_1 + n_2 \cos \theta_1}^2 \quad (6)
\]
The type of polarization indicates that the electromagnetic waves at the interface have an electric field component that is either parallel (p-polarized) or perpendicular (s-polarized) to the plane of incidence which in Figure 1 is the plane that is parallel to the page. When considering Snell’s Law, the incident and transmitted (refracted) angles can be related, i.e. \( \frac{\sin \theta_i}{\sin \theta_t} = \frac{n_2}{n_1} \) such that with a little inspection, equations 5 and 6 show that as the refractive index of \( n_2 \) gets closer to \( n_1 \), the reflectivity decreases. This is observed in Figure 3 by simply comparing spectra resulting from polyethylene only and silicon carbide only.

The certificate of analysis of the silicon carbide suggests that the SiC powder may contain a small amount (<.75%) of carbon black. Carbon black is found in automobile tires and absorbs light at all wavelengths [6]. The refraction indexes that we consider for our system are: Silicon Carbide, 2.55 [7]; Polyethylene, 1.51 [8]; Carbon Black, 1.84 [9]; Toluene, 1.50 [10]; Zinc Selenide (diamond), 2.3 – 2.7 [11]; Air: 1 [12]. Note that SiC and ZnSe have nearly matching refraction indices. Figure 3 shows the spectrograph of a pure polyethylene composite along with a pure SiC powder spectrograph. The SiC powder has a higher refractive index than polyethylene resulting in a slant to the entire graph. It can be noted that there is no signature of surface phonon-polariton activity in the polyethylene but there is a dip in the SiC powder around the range of 763-996 cm\(^{-1}\).

In Figure 3, the change in the relative refraction index is accomplished by changing material, but alternatively, we recognize that the nanocomposite refraction index can change if one of its component materials is removed. In Figure 4, our results for a five day kinetics study (e.g. 10:1 mass ratio) are shown for the spectral region matching the phonon-polariton coupling. In the kinetics study, the toluene evaporates each day, and the nanocomposite has an effective refraction index due to the remaining components, polyethylene and silicon carbide (and toluene). In addition, the refraction index becomes more like SiC and less like toluene so reasonably, the spectra progressively diminish toward the observed pure SiC. As the toluene in the composite evaporates, the graphs become lower and lower until days four and five. Note that the FTIR-ATR cannot directly measure changes in the composite refraction index. Figures 5 and 6 show the kinetics results for the

![Figure 3 Spectra of Polyethylene (top) vs. SiC powder (bottom). Highlighted region (right) is the location of surface phonon-polariton coupling.](image)

![Figure 4 Five day spectra averages for 10:1 mass ratio. As the toluene evaporates, reflectivity decreases at all wavenumbers including the region shown (i.e. the location of the surface photon-polariton response).](image)
other mass ratios. Although the other ratios (in Figures 5 and 6) do not appear to follow the same trend as the 10:1 recipe in Figure 4, there was more error observed. There was more variation in the first few days (Days 1 and 2) as the sample dried. When the error is accounted for in each graph based on the 10 sample spectra, the same %T decrease with drying time, a trend also exhibited by the 10:1 recipe, is observed. In all cases of mass ratio, the day 5 averages were the lowest in %T response. Figure 7 below shows the graph of the 10 samples that were taken on Day 5 for the 10:1 mass ratio. All of the samples’ signatures were relatively close to each other, thus, minimizing the error in the graph. As it can be seen in Figure 7, all of the day 5 ratios were centralized with only one or two spectra occurring higher than the mean. By averaging all of the day 5 graphs into one curve and comparing the different ratios on one graph in Figure 8, it can be seen that as the relative mass of polyethylene...
gets higher, the reflectance increases which is consistent with Figures 3 and 4.

Below are two sample SEMs for the 10:1 recipe. In Figure 9 (top), we see nanoparticle clustering based on an earlier mixing method. And in Figure 9 (bottom), we observe better mixing for the method used in this work. At high resolution, we determine clusters on the order of 200 nm with good mixing that are smaller than those observed previously.

4 Conclusion

Through the kinetics drying study we found out that as the composite dried, it’s signature on the FTIR become lower and lower. Five days was what was determined to be when the nanocomposites were considered dry based on the FTIR-ATR analysis. Each day the graph showed a decrease in reflectivity indicating that the composition of the nanocomposite changed as the toluene evaporated. Day five was shown to be when the graphs started to level out. We have also reported a study on the effects of inter-particle spacing on surface phonon-polariton modes in polyethylene/silicon carbide composites. A correlation was found between the distances of the nanoparticles and the polariton resonances which helped to create a ladder. The surface phonon polariton modes were found between the wavelengths of 763 to 996 cm\(^{-1}\) throughout all of the mass ratios as predicted but the total reflectance of the infrared radiation grew as the ratios converged to a 5 to 1 mass ratio of polyethylene to silicon carbide. We have provided an effective way of making nanocomposite with adequate mixing of the nanoparticles and polyethylene to provide equal spacing of the nanoparticles throughout the composite.

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