Phase selectivity of microwave heating evidenced by Raman spectroscopy

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Phase-selective temperature evolution of silicon-diamond powder mixtures under 2.45 GHz microwave irradiation is followed using a Raman microscope fitted onto a microwave cavity. This spectroscopic method is shown to enable the collection of thermal information for both the silicon and the diamond phase selectively. An initial difference up to 100 °C is found between the thermal trajectories extracted from silicon and diamond. A thermal equilibration is observed, subsequently suggesting that heat is flowing from hot silicon towards the colder diamonds. The existence of microscopic thermal gradients reflects the specific interaction of each of the two components with the applied electromagnetic field, governed here by the free carrier concentration. In addition to phase-specific temperature measurements, monitoring of chemical changes during microwave heating is also illustrated for magnetite powder. Raman spectroscopy turns out to be a powerful contact-free, noninterfering tool to follow and analyze on-line microwave heating processing of heterogeneous solid mixtures. © 2006 American Institute of Physics. [DOI: [10.1063/1.2198931](https://doi.org/10.1063/1.2198931)]

I. INTRODUCTION

Microwave energy has been considered for heating of materials for about 50 years. Despite considerable advances in the design of applicators and microwave (MW) sources, monitoring of the thermal evolution of materials under MW environment is far from trivial and still remains a major challenge.^{1,2} The way MWs interact with matter depends mainly on the electrical conductivity, the complex permittivity, and the complex permeability of the materials. When powdered materials of strongly differing dielectric properties are mixed together and are submitted to MW radiation, the amount of thermal energy generated by the electromagnetic field is expected to be different in each of the phases. This phenomenon in which punctual heat sources are selectively activated has not yet been observed *in situ* due to the lack of suitable phase-selective temperature measurement techniques compatible with a MW field.

Among the contact-thermometric methods, traditional thermocouples are to be discarded for MW furnaces as they severely interfere with the electromagnetic field.³ On the other hand, nonmetallic optical fibers are insensitive electromagnetic fields and can be used in MW furnaces for temperature measurements based on IR pyrometry, fluorescence decay, or refractive index changes. However, the information collected is typically limited to the average temperature of the sample volume in direct contact with the probe. Remote IR thermography can evaluate a larger zone of the sample and reveal some macroscopic temperature heterogeneities. It relies on the temperature dependent IR emissivity of materi-

als which depends not only on the nature of the material probed but also on the takeoff angle and the roughness of the samples. Given the chemical changes occurring during the heating of reactive powder mixtures, an accurate evaluation of the temperature using thermography becomes quite complicated. Moreover, apart from the difficulty to evaluate the true temperature of a sample in a MW field with the above methods, none of these methods is able to evidence microscopic temperature heterogeneities between the individual components of a composite mixture.

In this work we show that during the selective MW heating of diamond-silicon powder mixture, the temperature of each individual component can be determined up to temperatures exceeding 700 °C by Raman spectroscopy. The ability of Raman spectroscopy to follow additionally chemical changes *in situ* is exemplified using the oxidation reaction of magnetite into hematite.

II. EXPERIMENT

The diamonds used are Si-coated MBS960Si2 (200–300 μm, coating thickness: 50–100 nm) from General Electrics. The silicon powder ($d_{10}=51.1$, $d_{50}=80.5$, and $d_{90}=113.3$ μm) is obtained by ball milling of intrinsic silicon followed by sieving and subsequent alkaline treatment to remove iron traces. The magnetite (98%, <5 μm) used was purchased from Aldrich.

The experimental setup used is shown in Fig. 1. MW heating is carried out in a WR-340 waveguide terminated with a sliding short circuit. The MW generator with a maximum power of 300 W at 2.45 GHz (Sairem, GMP 03 KSM) is coupled through a coaxial cable to the waveguide. The

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FIG. 1. (Color online) Experimental setup comprising a microwave source, a microwave reflectometer, a monomode microwave cavity, a Raman microscope, and an optical thermometer.

incident and reflected power is monitored using a high power impedance analyzer (Coher-Muegge MDIAH2450). For a better coupling and uniformity of MW heating, the sliding short circuit is adjusted to ensure that the samples are located at the maximum of the electrical field of the TE_{10} mode. Samples are inserted into a $\varnothing 10 \times 60$ mm quartz test tube and placed inside the resonant cavity through a nonradiating slot in the wider wall. For high temperature experiments, a thermal insulation (KVS164, RATH) surrounding the test tube is used to minimize the radiative losses.

The sample temperature is monitored by a fiber optic thermometer (FISO UMI-8, fitted with a FOT-L probe limited to 250°C) and by Raman spectroscopy. Raman spectroscopy measures phonon frequencies, and their temperature dependence is used to determine the temperature of materials in the MW cavity. Raman measurements are carried out using a Renishaw In Via micro-Raman system, equipped with a charge coupled device (CCD) detector and 488 nm excitation of an Ar^+ ion laser as excitation source. The Raman spectra are recorded in backscattering geometry using a $5\times$ microscope objective which, due to its long working distance, allows remote measurements of materials inside the MW chamber. The laser spot size lies in the $10\text{--}15\ \mu\text{m}$ range. The spectral shift resolution of the system is about $0.1\ \text{cm}^{-1}$. The power of the laser beam is kept inferior to 1 mW to avoid local heating effects in the powder samples. More details about the Raman thermometry technique can be found elsewhere.^{4,5} Figure 2 shows the temperature calibration used for the dominant phonon modes of Si and diamond. It is determined using a Linkham TS1600 heating stage in the temperature range between 20 and 1000°C . The resulting temperature resolution of Raman measurements is about $\pm 10^\circ\text{C}$ at 100°C , improving towards higher temperatures.

III. RESULTS AND DISCUSSION

A. Temperature measurements

The relation between the temperatures measured with the conventional optical probe and the Raman thermal probe is investigated first. Si-coated diamond powders are heated up to temperatures close to 250°C in 25°C steps by adjusting the incident MW power. A comparison of the signal from the optical probe inserted 15 mm below the surface of the powder bed and the Raman temperature is shown in Fig. 3.

FIG. 2. (Color online) Temperature dependence of the Raman shift for the dominant silicon and diamond phonon modes.

Raman temperature values remain always below the optical fiber temperature. A maximum difference of 25°C is observed in the $24\text{--}250^\circ\text{C}$ range, with better agreement at lower temperatures. Due to the absorption of the laser light in the Si-coated diamond powder, Raman probes predomi-

FIG. 3. (Color online) Comparison of temperature readings from optical and Raman thermal probes for Si-coated diamond powders. The Raman temperature is measured on the surface while the optical probe is inserted in the powder bed 15 mm beneath the surface.

FIG. 4. (Color online) Raman temperature evolution for a silicon-diamond powder mixture placed inside the microwave cavity under 25 W steps heating in air. The evolution of the applied microwave power is also displayed.

nantly the surface of the powder bed. The lower Raman temperature is consistent with the fact that the surface of the powder bed is expected to be colder than the sample core. The thermal gradient results from the combination of the radiative ($\sim T^4$) and convective thermal losses, more pronounced on the upper surface of the powder bed, associated with the generally low thermal conductivity of a powder (up to three orders of magnitude lower compared to bulk materials). The result illustrates the suitability of the Raman thermal probe for temperature measurements in a MW cavity, while it needs to be kept in mind that mainly the material surface is taken into account. Note that for powders the depth of laser light penetration will be limited by multiple reflection and refraction processes even for optically transparent materials. For optical nontransparent materials, i.e., for materials with a band gap smaller than the laser excitation energy, the penetration depth can be estimated by $1/2\alpha$ for the Raman process, α standing for the absorption coefficient. Varying the excitation wavelength allows us to change the probing depth. The penetration depth of the 488 nm impinging laser radiation used here lies in the order of a few hundreds of nanometers for Si.⁶

The above measurements are limited to 250 °C, due to the maximum temperature range accessible with the optical fiber probe. The use of the Raman thermal probe at significantly higher temperatures is illustrated in Fig. 4. The temperature evolution of a (50:50 vol %) mixture of coated diamonds and silicon powder submitted to MW irradiation in 25 W steps from 50 up to 300 W is reported. During the first 500 s the power is ramped up to 175 W. During the initial 250 s the temperature reaches about 600 °C for the Si component (T_{Si}) of the powder mixture, while the diamond component (T_D) only attains 500 °C. After 250 s both T_{Si} and T_D decrease with a minimum occurring at around 300 s prior to reaching a plateau, the MW power being hold at 175 W. After 800 s the MW power is again increased stepwise until it reaches 300 W (1300 s), maintained for 1000 s and then shut off. T_{Si} stays initially nearly constant during the ramping up of the MW power from 175 to 300 W, while T_D increases slightly towards T_{Si} , both temperatures rising after 1500 s,

FIG. 5. (Color online) Comparison of the heating behavior of pure silicon powder with that of pure uncoated diamond powder under similar microwave irradiation [incident power: 250 W, absorbed power: 50 W (silicon), <1 W (diamond)].

reaching nearly 750 °C for T_{Si} but only 690 °C for T_D . As the MW power is shut off, the temperature decreases for both subcomponents of the powder.

In general, silicon is heating faster and cooling slower than diamond during the experiment. This can be explained by the different physical properties of Si and diamond. Silicon and diamond are both nonmagnetic, homopolar, and isostructural $Fd3m$ crystals. The absence of any permanent dipole in both crystals excludes the dipolar relaxation heating mechanism. As the first lattice vibration frequencies lie for both far above 2.45 GHz [in the infrared region of 18 000 GHz for Si (Ref. 7)], the MW absorption is reduced to the interactions of the electromagnetic field with intrinsic and extrinsic free carriers. The intrinsic carrier concentration for a given material depends on the magnitude of its band gap with respect to the available thermal energy (kT). Due to its wide band gap (5.45 eV), the population of thermally excited carriers in diamond remains negligible in the range of temperatures of interest here. Very little MW absorption is therefore expected in the diamonds. In contrast, for silicon, due to the smaller band gap of around 1.1 eV, a significant amount of thermal carriers is present. Indeed the real and imaginary parts of the permittivity were determined to be 3.08 and $<1 \times 10^{-4}$ for the uncoated diamonds and 7.41 and 1.15×10^{-1} for the silicon powder; the transparency of diamond and the moderate losses of silicon are confirmed in Fig. 5, showing that under the same MW irradiation conditions, the temperature of pure silicon powder rises rapidly whereas the temperature of pure uncoated diamonds remains unchanged.

As the temperature rises, more free carriers are generated and the conduction losses in Si become significant. This phenomenon essentially accounts for the higher MW absorption and faster heating behavior of Si compared to diamond up to 300 s. The diamonds in turn are indirectly heated via heat transfer from the silicon and to a negligible extent from direct MW absorption.

In the heating trajectory, a plateau approaching 600 °C is observed between 500 and 1500 s, despite the rising of the carrier concentration in silicon and that of the incident MW power. This behavior can be explained considering the contribution of the MW reflection, the changes in the MW penetration depth, and the radiative thermal losses. The penetration depth D_p of the electromagnetic field in bulk silicon has been shown to be inversely proportional to the electric conductivity,⁸

$$D_p = \sqrt{\frac{2}{\omega \mu \sigma}}, \quad (1)$$

while the MW reflectivity Γ is proportional to the electric conductivity of the sample,⁹

$$\Gamma = \frac{\eta - \eta_0}{\eta + \eta_0}, \quad (2)$$

where

$$\eta = \sqrt{\frac{\mu}{\varepsilon - i(\sigma/\omega)}}, \quad (3)$$

and

$$\eta_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}}. \quad (4)$$

σ , μ , and ε are the conductivity, permeability, and permittivity of Si, respectively, μ_0 and ε_0 stand for the permeability and the permittivity of free space, respectively, and ω is the angular MW frequency. As the temperature rises radiative thermal losses increase as a function of T^4 according to the Stefan-Boltzmann law. In addition, the fraction of incident MW reflected on the surface of the sample increases, while the absorption of the remaining MW tends to take place nearer to the sample surface. Consequently the total amount of electromagnetic energy converted to thermal energy by the powder bed recedes. For silicon, a self-limited heating therefore takes place, resulting in a slowdown of the temperature uptake despite the increasing MW power. While Si is maintained at a dynamic thermal equilibrium, heat flows towards the diamonds, presenting a lower thermal capacity ($\sim 470 \text{ J kg}^{-1} \text{ K}^{-1}$ at 300 K) but higher thermal conductivity ($\sim 1500 \text{ W/mK}$ at 300 K) than silicon ($\sim 700 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\sim 150 \text{ W/mK}$ at 300 K) until the temperature equalizes in both materials after 1500–1700 s. The final temperature uptake of silicon after 1500 s is attributed to plasma generation inside the powder bed. As the intensity of the applied electromagnetic field increases above the threshold equivalent to the work function of electrons in Si, discharges are expected between the “metallic” Si grains,¹⁰ explaining a further increase in temperature. As MW irradiation is ceased after 2200 s, the diamonds cool down faster as the silicon, again due to the higher thermal conductivity and lower thermal capacity of diamond.

The temperature dip occurring during the initial stage of heating at about 300 s has not been discussed so far. It may be assigned to a transient mismatch between the incident MW field and the sample, since its dielectric properties are

FIG. 6. *In situ* Raman spectroscopy of magnetite powder under constant microwave irradiation (25 W). (1) starting magnetite, (2) intermediate phase, (3) and (4) formation of crystalline hematite, and (5) crystalline hematite after cooling to room temperature.

expected to change while under heating, but other factors such as mechanical settling down of the powder might also intervene.

B. Chemical evolution

To illustrate that not only temperature but also chemical information can be extracted *in situ* using the Raman method, the oxidation of magnetite Fe_3O_4 to hematite ($\alpha\text{-Fe}_2\text{O}_3$) by heating under air was followed. Due to its magnetic properties, magnetite is a well known MW absorber. The Raman evolution of magnetite under constant MW irradiation (25 W) is shown in Fig. 6. As the MW irradiation starts the phonon mode around 660 cm^{-1} (A_{1g}), characteristic for Fe_3O_4 , disappears [spectrum (2)], suggesting the formation of an intermediate amorphous iron oxide. As the MW irradiation is continued, broad shoulders at 410 and 500 cm^{-1} form before the characteristic Raman doublet of hematite appears at $218/285 \text{ cm}^{-1}$ [$A_{1g}(1), E_g(2+3)$]. More details about hematite Raman modes can be found in Ref. 11. As the MW power is turned off the sample cools down [spectrum (5)]. The position of the measured Raman peaks gradually shifts to their room temperature values ($225/294 \text{ cm}^{-1}$). Applying a temperature dependence of about $0.015 \text{ cm}^{-1} \text{ K}^{-1}$ for the hematite $A_{1g}(1)$ mode,¹¹ the temperature at which the formation of hematite occurs is found to be around $500\text{--}600 \text{ }^\circ\text{C}$. This estimated temperature is somewhat lower than the $700\text{--}800 \text{ }^\circ\text{C}$ reported in conventional heating;¹² however, care should be taken due to the low accuracy of the temperature coefficients reported for hematite. The difference in peak intensity in the Raman spectrum between both compounds, i.e., the magnetite and the hematite, is due to hematite having a much stronger Raman scattering cross section compared to magnetite.

IV. CONCLUSION

In this work, a method for noncontact temperature measurements during MW irradiation has been demonstrated. Beyond infrared thermography or optical thermometry, the

use of Raman spectroscopy allows obtaining temperature information from each individual phase of a heterogeneous sample. The existence of microscopic thermal gradients in a composite can be evidenced and used to distinguish between several heating mechanisms, resulting either from direct MW absorption or interphase heat conduction. Applicable from very low to very high temperatures, Raman spectroscopy possesses assets of particular significance for the understanding of MW assisted materials processing. Moreover, the simultaneous access to transient temperature and chemistry offers a powerful tool for the clarification of the controversies about “microwave effects.”

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