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Apparatus for processing of samples at high pressures and high temperatures in a fast quenching-rate regime and synthesis of polyacetylene by pulsed laser heating of confined carbon thin films

M. L. Andreazza,^{1,2} C. A. Perottoni,^{1,2,a)} and J. A. H. da Jornada^{2,3}

¹Universidade de Caxias do Sul, 95070-560 Caxias do Sul-RS, Brazil

²Universidade Federal do Rio Grande do Sul, Instituto de Física, 91501-970 Porto Alegre-RS, Brazil

³Inmetro - Instituto Nacional de Metrologia, Normalização e Qualidade Industrial, 25250-020 Xerém-RJ, Brazil

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The pulsed laser heating of confined samples followed by ultrafast cooling constitutes an interesting route to explore the production of new phases and compounds. Indeed, in some cases the ultrafast cooling allows retaining at ambient conditions species that were produced under extreme conditions. The experimental setup described in this work allows the heating of thin film samples to temperatures ranging from 1400 to 5500 K, in a controlled and measurable way, with estimated cooling rates in excess of 10^{11} K·s⁻¹. In this paper, we show that the pulsed laser heating of thin amorphous carbon films deposited on copper substrates leads to the formation of polyacetylene in peak temperatures ranging from 1400 to 2600 K and static pressures between 0.8 and 1.1 GPa. The probable source of hydrogen was tracked to the small amount of water physically adsorbed at the carbon film/copper gasket interface. Because of the fast heating and cooling rate in these experiments, the hydrogen formed by water dissociation at high temperatures does not have enough time to diffuse out of the reaction cell. The results here reported strongly suggest that the evolution and stability of carbon-rich species produced by pulsed-laser heating at high pressure and high temperature critically depends on the capability of hydrogen retention in the reactional system. © 2011 American Institute of Physics. [doi:10.1063/1.3561501]

I. INTRODUCTION

Laser heating has emerged as an important tool for processing materials, yielding a variety of different phases at high temperatures and, in some cases, high pressures.^{1,2} When the conditions are such as to provide ultrafast cooling, nonequilibrium phases may be retained metastably at ambient conditions, a widely known example being the production of fullerenes.³ In fact, this molecular form of carbon was originally produced in a low density expanding carbon vapor in a helium atmosphere, which provides a very high cooling rate, thus precluding the formation of graphitic phases.

Recent studies based on molecular dynamics simulations have shown that carbon chains can be formed during the fast cooling of gaseous phases subjected to pulsed laser heating or combustion at temperatures up to 2400 K (Refs. 4 and 5). In these studies, the products obtained depend on the composition of the precursor, particularly the proportion of carbon to hydrogen (C:H) in the reactants. Of particular interest is the formation of polycyclic aromatic hydrocarbons (PAHs) from C₂H₂, C₂H₄, and C₆H₆ precursors. Depending on the conditions under which the heating and cooling of the gaseous carbon- and hydrogen-rich phases occur, it is possible to form even more complex structures, such as fullerenes and nanotubes.^{5,6} Evidences of hydrocarbons produced at high temperatures, particularly trans-polyacetylene (trans-PA), have also been observed in nanodiamond films growth by chemical vapor deposition (CVD) in hydrogen-rich environments.^{7,8}

The fact that polyacetylene has been identified in the grain boundaries of CVD diamond is noteworthy, as polyacetylene is known to decompose at temperatures well below that of the CVD substrate.⁹

In a previous work a carbon-based material was produced by processing of amorphous carbon films (a-C) deposited on a copper substrate with nanosecond Nd-YAG laser pulses.¹⁰ The Raman spectrum of that carbon material was very similar to that of polyacetylene but a conclusive identification of the product and the source for hydrogen was not accomplished at that time. Also, in that preliminary study, the static pressure and peak temperature at the surface of the laser-heated sample were only roughly estimated.

In this work, further evidences are presented that allow a positive identification of polyacetylene as the main product of pulsed laser heating of carbon films in a confined environment in the presence of hydrogen. Relatively simple and ubiquitous equipments were assembled together into an experimental setup that allows the experimental determination, *in situ*, of the static pressure and peak temperature at the surface of samples heated by a single laser pulse. A theoretical model was applied to estimate the quenching rate in experiments conducted with amorphous carbon films deposited on copper gaskets.

The experimental determination of peak temperature in pulsed laser heating is complicated by the rapid rise and fall of thermal radiation generated by nanosecond laser pulses. Typically, the sample warm up time is roughly the same as the temporal width of the laser pulse, while the cooling time depends mostly on the boundary conditions to which the

^{a)}Electronic mail: caperott@ucs.br.

sample is subjected.¹¹ Accordingly, the sensor device must have high sensitivity in order to detect the ordinarily faint thermal radiation emitted by sample during these fast heating and cooling processes.

Despite these difficulties, the determination of peak temperature in samples heated by nanosecond laser pulses has already been accomplished since, at least, the mid-eighties.¹² In fact, peak temperature of samples heated by pulsed lasers can be determined using gated detectors or by the use of a high pulse repetition rate, so that the thermal signal can be obtained by integration of some thousand pulses. This latter solution is described by Rekhi, Tempere, and Silvera, who applied it to the determination of the pressure dependence of iron and platinum melting points.¹³ However, in that work the quenching time was in the range of microseconds. This approach does not apply to the situation described in this work, where we are interested in the peak temperature reached by a sample heated by a single, nanosecond laser pulse, with cooling time of a few nanoseconds.

In the experimental setup developed for this work, peak temperatures can be measured up to around 5500 K, and the confinement of thin film samples inside the high-pressure cell provided quenching rates estimated to be around $10^{11} \text{ K}\cdot\text{s}^{-1}$. This fast cooling considerably reduces the time available for hydrogen diffusion out of the system, thus making it possible to quench hydrogen-rich species formed in the hot, dense gas confined under high pressure and generated by the high power density, nanosecond laser pulse.

II. EXPERIMENTAL PROCEDURES

The device used in this work to generate high static pressures, the sapphire anvil cell (SAC), was based on the diamond anvil cell (DAC) designed by Piermarini and Block.¹⁴ Although the SAC does not allow the generation of the same extreme static pressures attainable by the DAC, it has some characteristics that make it well suited to the study of laser-heated carbon films, including the low cost and the absence of carbon in the composition of the anvils.

Owing to the intervening fluorescence of the sapphire anvils, the ruby technique could not be used for the determination of the static pressure in the SAC. Instead, $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$ was used as pressure gauge.¹⁵ The excitation of the $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$ most intense fluorescence peak at 685.395 nm was accomplished by using a 10 mW He-Ne laser (Melles Griot 05-LHP-991). The $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$ fluorescence peak shifts with pressure by 2.55 nm/GPa.¹⁵ The static pressure was measured *in situ* before each processing with pulsed laser.

A low-pressure physical vapor deposition (PVD) chamber was used for the deposition of diamondlike amorphous carbon (DLC) films on composite copper gaskets. These are made of a Waspaloy foil sandwiched in between two copper foils. This composite gasket allowed the generation of higher static pressures without failure of the anvils. Furthermore, the copper surface also provides a very fast cooling rate, as well as an inert environment for hydrogen. The same Nd:YAG laser used to process the carbon films within the SAC was employed to produce the films by laser ablation of a rotating graphite target.¹⁰

A standard procedure was used in the preparation of the gaskets and the deposition of the carbon film. The former were submitted to a careful cleaning process to assure that they had always the same superficial texture and were free from oxidation and other contaminant substances on the surface. A valve in the PVD chamber enabled the gaskets to be controllably exposed to different ambient conditions before or during the carbon film deposition. The DLC nature of the carbon films as-deposited on the copper gaskets was characterized by Raman spectroscopy.¹⁶ The thickness of the carbon film as deposited was estimated by atomic force microscopy (Nanoscope IIIa, Digital instrument Co.) as $68 \pm 3 \text{ nm}$.

The samples were analyzed by micro-Raman spectroscopy. The spectra were excited by a HeNe laser at 632.8 nm, and the scattered radiation, collected with the aid of an Olympus BH-2 microscope, was dispersed by a Jobin-Yvon HR320 monochromator. A Jobin-Yvon T90000 Raman system, equipped with an argon laser at 514 nm and a triple spectrometer, was also used to observe the effect of the wavelength of the excitation laser on the Raman spectra. Both Raman spectrometers were equipped with liquid nitrogen-cooled CCDs for spectrum acquisition.

Figure 1 illustrates the experimental setup used for pulsed laser heating of samples submitted to high pressures in the SAC. The Nd:YAG laser used in this work (Spectra-Physics Quantum-Ray GCR-170) operates at 1064 nm, with 8.5 ns pulse duration (full width at half maximum) and pulse energy from about 18 up to 540 mJ. For the calculation of the power density at the sample surface in the laser heating experiments, the spot area at the focal point was obtained assuming a Gaussian radial profile and a radius corresponding to $1/e^2$ of the maximum intensity. Pulse energy was determined using an energy meter (FieldMaxTM II-P, Coherent Inc.).

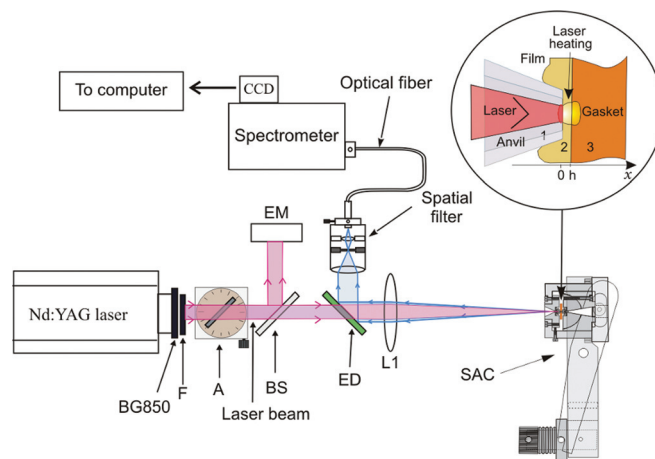


FIG. 1. (Color online) Schematic representation of the experimental setup used for processing and peak temperature measurement in laser heating experiments conducted with thin film samples confined under high pressure in a sapphire anvil cell (SAC). EM is the laser pulse energy meter, BG850 is a bandpass filter, F an attenuating filter, A is an adjustable attenuator, BS a beam-splitter, ED a dichroic mirror, and $L1$ is a focalizing lens with long working distance. The inset shows a detail of the sample inside the SAC. In the inset, 1, 2, and 3 refers to the three-layer mathematical model (which takes into account the effects due to the sapphire anvil, carbon thin film of thickness h , and copper gasket) used to estimate the quenching rate at the sample surface.

Peak temperature at the sample surface heated by a single nanosecond Nd:YAG laser pulse was estimated by fitting a Planck curve to the radiation spectrum.¹⁷ The same optical setup used to focus the laser light on the sample was used to capture the thermal radiation from the sample, as represented in Fig. 1.

High quenching rates in pulsed laser heating of thin samples confined under high pressure was made possible by the boundary conditions imposed by semi-infinite walls of high thermal conductivity materials. Owing to the impossibility of measuring the temperature decay in the sample surface with the available experimental setup, in this work the cooling rate was estimated by numerically solving a set of differential equations subjected to the boundary conditions dictated by the walls that confine of the sample inside the SAC. A step toward a better estimation of peak temperature and quenching rate consisted in the development of a three-layer model (sapphire anvil – carbon film – copper gasket), which included the effect of the sapphire anvil and also took into account the energy absorption across the carbon film.¹¹ This theoretical model allowed the determination of the quenching rate, around $10^{11} \text{ K}\cdot\text{s}^{-1}$, which was defined as the time needed to reduce the film surface temperature to half peak temperature. This fast quenching, about ten thousand times faster than those typically obtained with a melt spinner, is of paramount importance in determining the ability of the experimental setup in retaining species created at high temperatures and high pressures.^{18,19} Moreover, the fast cooling also reduces the time available for hydrogen diffusion out of the hot, dense gas mixture generated by the pulsed laser heating of the sample, allowing the retention of hydrogen-rich species formed under these conditions.

III. RESULTS AND DISCUSSION

The experimental setup for the measurement of temperature was validated by measuring the melting point of platinum and tungsten foils at ambient pressure. The sample of tungsten was kept under a flow of pure nitrogen gas to avoid oxidation. Melting of the metal samples is signaled by a distinct dwell in the peak temperature versus laser power density plot. The measured melting points, 2100 and 3630 K for platinum and tungsten, respectively (with an uncertainty of about 150 K) are in very good agreement with the literature (2045 and 3680 K for platinum and tungsten at ambient pressure, respectively).²⁰

Figure 2 exhibits a comparison between a Raman spectrum typical of the samples produced by fast heating and cooling of carbon films deposited on copper gaskets and confined under pressure in the SAC, already described in a previous work,¹⁰ and that of a chemically prepared polyacetylene film. The very good agreement between both spectra allows the unambiguous identification of the carbonaceous species previously reported as polyacetylene. In fact, the Raman spectrum at the bottom of Fig. 2 exhibits all main peaks assigned to trans-PA, along with a minor peak due to the cis isomer. Moreover, the analysis of the Raman spectra excited with different lasers showed that the dispersion of the peaks at 1100 and 1498 cm^{-1} , for the species obtained by pulsed laser heating of amorphous carbon films, is consistent with

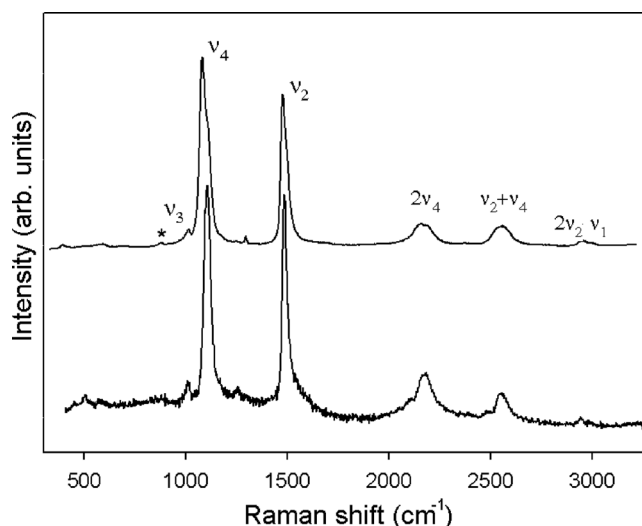


FIG. 2. Raman spectra of the sample produced by laser heating at high pressure, in the SAC, of a thin carbon film deposited on copper (below) and of a trans-polyacetylene film prepared by a standard chemical method, with some assigned bands (top). The asterisk marks the position of a Raman peak from cis-PA.

the dispersion of the Raman v_2 and v_4 modes of trans-PA. The same applies to the dependence of the intensity ratio v_4/v_2 with the wavelength of the excitation laser.

The shift of the Raman peaks associated to the species produced in the SAC with respect to trans-PA, namely from 1060 to 1100 cm^{-1} in the case of the v_4 mode, and from 1460 to 1498 cm^{-1} for the v_2 mode, can be ascribed to the size of the carbon chain. In fact, it is well known that peak positions in the Raman spectrum of polyacetylene depends on the number of conjugated carbons present in the chain.^{21,22} Accordingly, it can be estimated that around 30 carbon atoms are present in trans-PA produced by pulsed laser heating of carbon films confined in the SAC. For comparison, in the chemically prepared trans-PA film, whose Raman spectrum is depicted in the top of Fig. 2, the mean chain length can be estimated around 60 carbon atoms. The greater chain length in the trans-PA film is consistent with the synthesis conditions and the longer time available for the polymer to grow.

A Raman spectrum typical of trans-PA was observed in thin amorphous carbon films processed with laser pulses, with peak temperatures from 1400 to 2600 K , under static pressures between 0.8 and 1.1 GPa .

Polyacetylene, $(\text{CH})_n$, is a hydrogen-rich hydrocarbon, so it is important to clarify the probable source of hydrogen in our experiments. With this aim in mind, a series of controlled experiments allowed us to observe that the water vapor pressure to which the copper gasket was exposed has an influence on the formation of polyacetylene. To further explore this influence, the copper gaskets were exposed to an environment with different partial pressures of water vapor, in the PVD chamber, before the amorphous carbon film deposition. According to the results thus obtained, the maximum yield for polyacetylene production was observed for copper gaskets exposed to a water vapor pressure of about 0.53 Pa just before the carbon film deposition.

According to the findings here reported, the water adsorbed in the copper gasket/carbon film interface may be

the source of hydrogen for the synthesis of polyacetylene. The confinement of the thin carbon sample between the sapphire anvil and the copper gasket, and the fast processing with nanosecond laser pulses effectively provides the hydrogen-rich environment needed to allow the synthesis of polyacetylene from a very hot gaseous mixture of carbon and hydrogen species. We assumed at first that a very rapid cooling was necessary to preclude decomposition of the polyacetylene chains formed in the dense, hot gaseous mixture generated by the laser pulses. However, a most fundamental reason for the successful synthesis of PA in our experiments is that the fast heating and cooling process provided by the laser pulse and the high thermal diffusivity of the materials around the sample drastically reduces the time available for hydrogen diffusion out of the system. In fact, the confinement of the sample in the SAC provides the conditions for the formation of a dense, hot, hydrogen-rich gaseous mixture where polyacetylene and related carbon compounds may actually be stable species.

Polyacetylene synthesized by conventional chemical routes decomposes above 690 K under inert gas or vacuum, which is preceded by cross-linking reactions that begin at even lower temperatures.⁹ The anomalous stability of trans-polyacetylene found in the grain boundaries of CVD diamond growth over substrates heated above 980 K has been attributed to some kind of rearrangement of the molecular structure.^{7,8} However, our results suggest an alternative explanation, i.e., that polyacetylene should be stable in a carbon- and hydrogen-rich environment under high pressure and high temperature.

To further validate this conclusion, a sample of thin polyacetylene film, produced by standard chemical methods, was subjected to the same processing conditions as the carbon thin films, i.e., pulsed laser heating at high pressure inside the SAC, in a confined environment that is essentially impervious to hydrogen diffusion during the heating and cooling cycle. The Raman spectrum of the processed sample was essentially identical to that of the pristine sample, in spite of the high temperature reached by the sample during laser processing. Of course, kinetic aspects related to phase transformation should also be taken into account when interpreting these results. Nevertheless, the apparent stability of polyacetylene suggested by our experiments and also by the observation of PA in the grain boundaries of CVD diamond, points to the need to further explore the thermodynamic stability of hydrocarbons in hydrogen-rich environments at high pressures and high temperatures.

IV. CONCLUSIONS

A simple experimental setup was devised to perform pulsed laser heating of samples confined under high pressure inside a sapphire anvil cell. Peak temperature was estimated by fitting a Planck curve to the measured spectrum of the thermal radiation emitted by the sample. This procedure was validated by measuring the platinum and tungsten melting temperatures. This device enabled the processing with nanosecond pulsed laser of thin amorphous carbon films confined under pressures and temperatures up to 5 GPa and 5500 K, respectively. Furthermore, the confinement of thin film samples inside the sapphire high-pressure cell provided the conditions for the attainment of quenching rates in excess of $10^{11} \text{ K} \cdot \text{s}^{-1}$. This

fast quenching effectively reduces the time available for hydrogen diffusion out of the system, in such a way that makes possible to explore the production and stability of hydrogen-rich species formed in the hot, dense gas confined under high pressure and generated by nanosecond laser pulses.

This apparatus was used to study the formation and stability of polyacetylene formed in experiments of laser heating of thin carbon films deposited on copper. A Raman spectrum typical of trans-polyacetylene was observed in thin amorphous carbon films heated from 1400 to 2600 K under static pressures between 0.8 and 1.1 GPa.

The high reactivity and diffusivity of hydrogen makes it difficult to carry out experimental studies on polyacetylene stability in hydrogen-rich environments under static conditions. The apparatus described in this work, on the other hand, is especially suited for such studies under transient conditions and provides an interesting alternative to explore the production and stability of polyacetylene and related species at high pressures and high temperatures. Furthermore, with some minor modifications the experimental setup described in this work can also be used, for instance, to experimentally explore details of the physical-chemistry of hydrocarbon combustion in confined environments.

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