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Influence of ambient gas on the temperature and density of laser produced carbon plasma

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The effect of ambient gas on the dynamics of the plasma generated by laser ablation of a carbon target using 1.06 μm radiation from a Q-switched Nd:YAG laser has been investigated using a spectroscopic technique. The emission characteristics of the carbon plasma produced in argon, helium and air atmospheres are found to depend strongly on the nature and pressure of the surrounding gas. It has been observed that hotter and denser plasmas are formed in an argon atmosphere rather than in helium or air as an ambient. © *1998 American Institute of Physics.* [S0003-6951(98)04102-3]

The interaction of laser ablated carbon plumes with background gases is currently receiving considerable attention because of its importance in understanding the dynamics of cluster formation[1–3] and diamond-like carbon (DLC) thin film growth.[4–6] Despite the significant success that has been achieved in the preparation of DLC thin films and in the production of higher carbon clusters using laser ablated carbon plasma, detailed aspects of the dynamics of laser induced plume expansion into an ambient gas are not fully understood. Compared to the expansion into a vacuum, the interaction of the plume with an ambient gas is a far more complex gas dynamic process which involves deceleration, attenuation, thermalization of the ablated species, and formation of shock waves.[7] Recent measurements performed over a wide range of expansion durations have demonstrated a fairly complicated gas dynamic picture of plume ambient gas interaction which is characterized by different propagation phases and is accompanied by plume oscillations arising at rather high background pressures.[8–11] Due to the complexity of the ablation dynamics, an appropriate theoretical description of plume expansion applicable for a wide range of ablation conditions is lacking. In low gas pressure, the plume propagation could be described by Monte Carlo simulation.[12] In moderate or high pressures, a blast wave model is found to describe accurately the plume propagation distance during the early expansion stages, whereas a shock layer model and an empirical drag model predict the maximum plume length with considerable accuracy.[7,13]

In this letter we report the effect of ambient atmosphere on the laser vaporization and excitation processes which were investigated using a spectroscopic technique. Studies were made by keeping the graphite target in three different atmospheres viz. air, helium and argon, with pressures ranging from 1 mbar to 10^{-5} mbar.

Details of the experimental techniques employed here are given elsewhere.[14] Briefly, plasma was generated by laser ablation of the high purity graphite sample, placed in an evacuated chamber, using 1.06 μm radiation pulses from a Q-switched Nd:YAG laser with a repetition rate of 10 Hz. The estimated spot size at the target was 200 μm. The bright plasma emission was viewed through a side window at right angles to the plasma expansion direction. The section of the plasma was imaged onto the slit of a 1 m Spex monochromator using appropriate collimating and focusing lenses so as to have one to one correspondence with the sampled area of the plasma and the image. The recording was done by using a thermoelectrically cooled photomultiplier tube, which was coupled to a boxcar averager/gated integrator. The averaged output from the boxcar averager, which for the present study averaged out intensities from 10 pulses, was fed to a chart recorder.

The electron density (n_e) was measured by the Stark broadening method, and electron temperature (T_e) of the carbon plasma was measured by the relative intensities of the successive ionization states of the carbon atom, the details of which are given in an earlier paper.[14] Recently we have reported the variation of T_e and n_e with different experimental parameters like distance from the target surface, time after the elapse of the laser pulse, laser irradiance, etc.[14] The variation of T_e and n_e with distance (z) shows $z^{-0.1}$ and z^{-1} dependences, respectively. The temporal dependence of these parameters gives a t^{-2} variation. It is also noted that at higher irradiance levels a saturation phenomenon is observed for T_e and n_e due to the formation of a self-regulating regime due to the interaction of the plasma with the trailing portion of the laser pulse.

The emission spectra, electron temperature and density are found to be significantly influenced by the ambient atmosphere. The addition of an ambient gas enhances the emission from all species. The relative enhancement depends on the nature of the gas, gas pressure and also the excitation energy of the electronic transition responsible for the line. The lifetime of all the transitions studied is of the order of a few nanoseconds, while the observed increase of the emission occurs within a time interval of the order of a few tens of nanoseconds;[9,15,16] the increase in intensity should be due to species that have been excited during the plasma expansion. The two main mechanisms invoked in the excitation are the particle collision excitation and the electron impact excitation.

Figures 1 and 2 give the variations of electron tempera-

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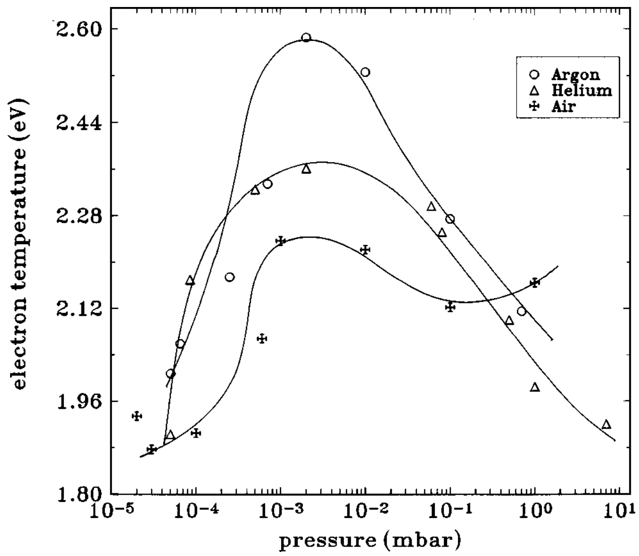

FIG. 1. Variation of electron temperature as a function of ambient pressure.

ture and electron density of the carbon plasma with pressure at three different ambient atmospheres (Air, He and Ar). These measurements were taken at a distance of 3 mm from the target surface and at a laser irradiance of 50 GW cm^{-2}. It is noted that the electron density shows a decreasing trend with an increase in pressure irrespective of the nature of the ambient gas used while the electron temperature shows a somewhat different behavior with respect to the nature and pressure of the ambient gas.

The three different laser intensity thresholds for plasma initiation in the presence of an ambient gas can be distinguished as the surface vaporization threshold, the target vapor plasma threshold and the ambient gas plasma threshold. These threshold values for vaporization, vapor plasma and gas breakdown strongly depend on experimental parameters like target material, wavelength of the laser radiation, nature of the ambient gas, etc. The shielding effect, i.e., the absorption of the laser energy by the plasma, strongly depends on nature of the background gas used. Ambient gas breakdown will profoundly influence the laser energy coupling to the target surface. If gas breakdown occurs before laser light reaches the sample surface, a major part of the energy will be absorbed by the resulting plasma formed from the gas. The laser irradiance used in these studies is 50 GW cm^{-2}. The breakdown thresholds of helium and argon reported using a Q-switched ruby laser are 300 and 100 GW cm^{-2} at atmospheric pressure and increase gradually with a decrease in gas pressure.[17] In the present work, the pressure range used for Ar and He is well below atmospheric pressure and one may safely predict that gas breakdown will not occur.

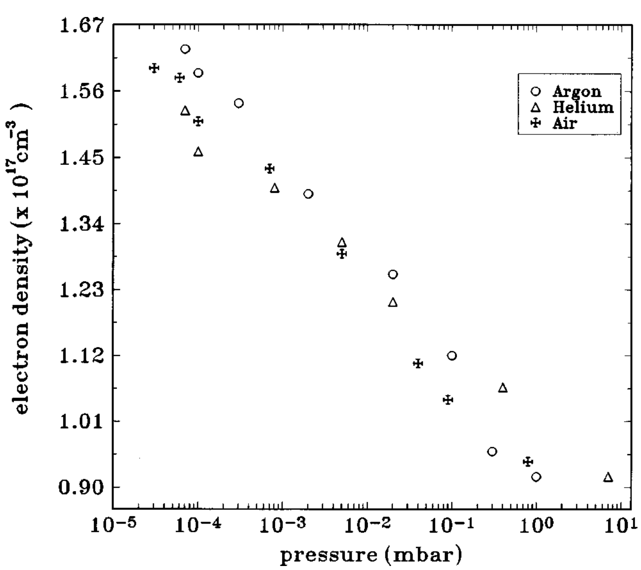

FIG. 2. Variation of electron density as a function of ambient pressure.

A cascade growth of the electron number density and absorption coefficient of the plasma will be greatly influenced by the nature of the background gas. The condition necessary for the development of cascade like growth is given by[18,19]

$$\frac{d\epsilon}{dt}=\frac{4\pi^2e^2I\nu_{\text{eff}}}{m_e c\omega^2}-\frac{2m_e\nu_{\text{eff}}E}{M}>0, \tag{1}$$

where ϵ is the energy of the free electrons; e and m are the charge and mass of the electron; M, the mass of the background gas neutral particle; E, the energy of the first ionization stage of the gas; ν_{eff}, the effective frequency of electron-neutral collision; I, the radiation intensity; and ω, the cyclic frequency of radiation. The first term on the right-hand side of Eq. (1) expresses the rate of growth of energy by the absorption of laser photons, and the second term gives the maximum rate of energy loss due to elastic and inelastic collisions with neutral gas particles. We have noticed that the absorption due to inverse bremsstrahlung is negligibly small at low irradiance levels and increases exponentially with increasing laser irradiance.[14]

When the plasma medium absorbs a significant fraction of laser energy, a laser supported detonation wave will be formed. Under this condition the length of the plasma can be written as[20]

$$z=\text{const}\left(\frac{E_F^2\sigma(\gamma^2-1)}{\rho\beta}\right)^{1/5}t^{3/5}, \tag{2}$$

where E_F is the electric field strength; γ, the specific heat ratio; ρ, the density of the ambient gas; β an absorption factor; and σ, the high frequency conductivity which is given by $\sigma=e^2n_e\nu/[m_e(\nu^2+\omega^2)]$, where ν is the electron collision frequency.[21]

At moderately high pressures, the plasma expansion can be modeled as a blast wave, which is represented by[20]

$$z=\left(\frac{W}{\rho}\right)^{1/5}t^{2/5}, \tag{3}$$

where W is the total energy absorbed. The dimension of the plasma, which is closely related to the density, temperature and coupling of laser radiation is influenced by the surrounding gas through Eqs. (2) and (3). We have noticed that the axial length of the plasma is considerably larger in helium atmosphere, especially at high pressures, in comparison with argon and air. This may be due predominantly to the lower density of helium than that of air[22] (taking the case of nitrogen) and argon.

In comparing argon and helium atmospheres, according to Eq. (1) the cascade condition is more favored for argon ($M=40, E=14.5$ eV) than He ($M=4, E=23.4$ eV). The plasma formed in Ar atmosphere is more absorptive than in He atmosphere and directly influences the value of T_e and n_e. We have observed that the temperature of the carbon plasma is higher in an argon ambient compared to those in the presence of helium or air.

It can be seen that the electron temperature attains a maximum value at $\sim 10^{-2}$ mbar for Ar and He ambient atmospheres, then decreases with a change of pressure. At pressures $>10^{-2}$ mbar, the T_e is found to decrease. But the electron density is found to decrease with an increase in pressure of the background gas irrespective of the nature of the buffer. As pressure increases, the confinement of the plasma nearer to the target surface takes place, which in turn increases the effective frequency of electron collisions with background gas atoms. The cascade condition is not favored at high pressures because of the energy loss due to elastic collision of the electrons with the neutral particles of the gas which supersedes the rate of growth of energy of free electrons via inverse bremsstrahlung. The increase in temperature up to 10^{-2} mbar can be explained as follows. As the pressure of the ambient gas increases, greater confinement of the plasma takes place, which enhances the elastic and inelastic collisions and thereby the recombination processes. This is supported by the fact that the increase in pressure decreases the electron density. The increase in temperature with pressure is therefore due to the energy gained by the recombinations superseding the cooling due to increased intraplume collisions.

It is noted that the temperature profile in air is different from the profiles in helium and argon particularly at high pressures. At high pressures ($\geqslant 10^{-1}$ mbar), with air as ambient, T_e shows an increasing tendency. T_e can be affected by chemical reactions in the plasma as well as by hydrodynamic expansions in the plasma. The nitrogen and oxygen present in the air atmosphere influence the temperature through exothermic reactions.[23]

The rate of change of electron temperature in the plasma is the sum of three terms viz., elastic collision, electron heating due to collisional deexcitation of metastable ions and recombination of ions. The rate of loss of electron energy at short times is mainly dominated by the elastic collision term $Q_{\Delta t}$, given by[24]

$$Q_{\Delta t}=\frac{2m_e}{M_B}\sigma_{ea}n_B\left[\frac{8kT_e}{\pi m_e}\right]^{1/2}, \tag{4}$$

where σ_{ea} represents elastic scattering cross section between electrons and atoms; n_B and M_B are the density and mass of background gas atom. From Eq. (4), the cooling is inversely proportional to M_B and hence lighter gases are efficient for rapid cooling. This confirms the recent result that the vibrational temperature of C_2 molecules decreases with increase in helium pressure.[2] Helium, being the lighter gas compared to Ar or N_2, gives rise to rapid cooling as is observed in the present experiment. Because of this helium gas is preferred as a buffer instead of air or argon for the preparation of fullerenes and the enhanced clustering phenomenon is favored in helium ambient.

In conclusion we have studied the effect of different ambient gases on the dynamics of laser ablated carbon plasma. The electron temperature and density show an abrupt change with the addition of ambient gases and these parameters also depend on the nature and composition of the gas used. It is noted that hotter and denser plasmas are formed in Ar atmosphere compared to He and air as a result of the difference in the efficiency of cascade-like growth of the electron number density and plasma absorption coefficient. However, contrary to He and Ar ambients, the temperature variation shows an increase at higher ambient air pressures suggesting T_e may be affected by chemical reactions as well as by simple hydrodynamic expansion of the plasma. The electron density exhibits a similar behavior irrespective of the background gas atmosphere. The inclusion of ambient atmosphere cools the hot electrons by collisions, leading to a more efficient electron impact excitation and plasma recombination, which lead to plasma confinement and in turn decrease of the electron density.

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[1] R. E. Smalley, Acc. Chem. Res. **25**, 98 (1990).
[2] S. S. Harilal, R. C. Issac, C. V. Bindhu, V. P. N. Nampoori, and C. P. G. Vallabhan, J. Phys. D **30**, 1703 (1997).
[3] S. S. Harilal, R. C. Issac, C. V. Bindhu, V. P. N. Nampoori, and C. P. G. Vallabhan, Plasma Sources Sci. Technol. **6**, 317 (1997).
[4] *Pulsed Laser Deposition of Thin Films*, edited by D. B. Chrisey and G. K. Hubler (Wiley, New York, 1994).
[5] D. H. Lowndes, D. B. Geohegan, A. A. Puretzky, D. P. Norton, and C. M. Rouleau, Science **273**, 898 (1996).
[6] A. A. Voevodin, S. J. P. Laube, S. D. Walck, J. S. Solomon, M. S. Donley, and J. S. Zabinski, J. Appl. Phys. **78**, 4123 (1995).
[7] D. B. Geohegan, Thin Solid Films **220**, 138 (1990).
[8] S. S. Harilal, R. C. Issac, C. V. Bindhu, V. P. N. Nampoori, and C. P. G. Vallabhan, J. Appl. Phys. **80**, 3561 (1996).
[9] S. S. Harilal, R. C. Issac, C. V. Bindhu, V. P. N. Nampoori, and C. P. G. Vallabhan, J. Appl. Phys. **81**, 3637 (1997).
[10] S. S. Harilal, R. C. Issac, C. V. Bindhu, V. P. N. Nampoori, and C. P. G. Vallabhan, Jpn. J. Appl. Phys., Part 1 **36**, 134 (1997).
[11] S. S. Harilal, P. Radhakrishnan, V. P. N. Nampoori, and C. P. G. Vallabhan, Appl. Phys. Lett. **64**, 3377 (1994).
[12] J. C. S. Kools, J. Appl. Phys. **74**, 6401 (1993).
[13] D. B. Geohegan, Appl. Phys. Lett. **60**, 2732 (1992).
[14] S. S. Harilal, C. V. Bindhu, R. C. Issac, V. P. N. Nampoori, and C. P. G. Vallabhan, J. Appl. Phys. **82**, 2140 (1997).
[15] S. S. Harilal, C. V. Bindhu, V. P. N. Nampoori, and C. P. G. Vallabhan, Appl. Phys. B (in press).
[16] S. S. Harilal, Ph.D. dissertation, Cochin University of Science and Technology, 1997.
[17] M. Young and M. Hercher, J. Appl. Phys. **38**, 4393 (1967).
[18] G. M. Weyl, in *Laser-Induced Plasmas and Applications*, edited by L. J. Radziemski and D. A. Cremers (Dekker, New York, 1989), Chap. 1.
[19] Y. Iida, Spectrochim. Acta B **45**, 1353 (1990).
[20] T. P. Hughes, *Plasmas and Laser Light* (Hilger, London, 1975).
[21] R. G. Root, in Ref. 18, Chap. 2.
[22] R. C. Weast, *CRC Handbook of Chemistry and Physics* (Chemical Rubber, Boca Raton, FL, 1988).
[23] S. S. Harilal, R. C. Issac, C. V. Bindhu, V. P. N. Nampoori, and C. P. G. Vallabhan, Spectrochim. Acta A **53**, 1527 (1997).
[24] P. T. Rumsby and J. W. M. Paul, Plasma Phys. **16**, 247 (1974).