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Nanomaterials synthesis at atmospheric pressure using nanosecond discharges

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The application of nanosecond discharges towards nanomaterials synthesis at atmospheric pressure is explored. First, various plasma sources are evaluated in terms of the energy used to include one atom into the nanomaterial, which is shown to depend strongly on the electron temperature. Because of their high average electron temperature, nanosecond discharges could be used to achieve nanofabrication at a lower energy cost, and therefore with better efficiency, than with other plasma sources at atmospheric pressure. Transient spark discharges and nanosecond repetitively pulsed (NRP) discharges are suggested as particularly useful examples of nanosecond discharges generated at high repetition frequency. Nanosecond discharges also generate fast heating and cooling rates that could be exploited to produce metastable nanomaterials.

Introduction

The unique physics and chemistry of plasmas presents numerous advantages for the fabrication of nanomaterials (Ostrikov 2005; Gonzalez-Aguilar *et al.* 2007; Ostrikov *et al.* 2007; Zheng *et al.* 2010). In particular, non-thermal plasmas have attracted much interest for the fabrication of various nanomaterials in low-temperature non-equilibrium conditions, such as nanocrystals (Kortshagen 2009). There is increasing interest in operating at atmospheric pressure, where high species densities may permit fast synthesis without vacuum systems. Focused research sub-topics have included the production of carbon-based nanostructures (Gonzalez-Aguilar *et al.* 2007; Nozaki *et al.* 2008) and the use of microplasmas (Mariotti *et al.* 2010). A detailed overview of plasma nanofabrication can be obtained from the aforementioned references, which are all review articles.

Scaling up plasma-based nanofabrication processes to the industrial scale is the primary motivation for improving their efficiency. Many methods consume excess energy and materials, largely because the fundamental processes involved are non-specific in nature. For example, many techniques involve heating the entire substrate to facilitate the surface reactions of the relatively few particles that participate in the assembly of a nanostructure. Non-thermal plasmas may provide the selective control needed to direct energy and matter efficiently.

In this article, we will compare the energy cost of synthesizing nanomaterials for various non-thermal plasma sources at atmospheric pressure. We will then argue that discharges of nanosecond duration hold significant promise for two reasons. First, they are capable of matching or surpassing the current benchmarks for nanofabrication efficiency. Second, the transient thermal processes produced by nanosecond discharges could be used to generate metastable nanomaterials.

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Energy cost per atom of nanomaterials synthesis

Here we compare the energy cost of incorporating each atom into the nanomaterial (ϵ_{atom}) for several case studies of nanofabrication using atmospheric pressure plasma sources, as shown in Table 1. For this comparison, argon at atmospheric pressure is used as the carrier gas for igniting the discharge in all cases. None use external substrate heating; synthesis results only from using the energy supplied by the plasma. Also, these particular studies provide both the discharge power (P) and the nanomaterial mass production rate (\dot{m}) necessary for calculating $\epsilon_{atom} = P / \dot{m}$. All of the nanomaterial produced is collected or at least accounted for when providing the mass production rate.

There are a few details concerning the calculation of ϵ_{atom} for each of the studies used in Table 1. For the microplasma used by (Nozaki *et al.* 2007), (Mariotti *et al.* 2010) estimates $\dot{m} = 1 \mu\text{g}/\text{min}$. For the microplasma used by (Shimizu *et al.* 2006), we calculate \dot{m} based on the given dimensions of the nanoparticle tower and the density of bulk WO_3 . For the spark discharge used by (Tabrizi *et al.* 2009), \dot{m} is equated to the rate of electrode mass loss. For the microwave (mw) torch used by (Dato *et al.* 2008), $\dot{m} = 2 \text{ mg}/\text{min}$ is the amount of solid carbon material collected, which is assumed here to be entirely made up of nanomaterial.

From Table 1, we see that no single plasma source emerges as the most efficient, with energy costs ranging from 1 to 600 keV per atom. Sparks, microplasmas, and mw torch sources are all capable of reaching the lowest energy cost of about 1 keV/atom. It is also not clear that we should expect similar performance from the same source, as evidenced by the wide range of energy costs for mw torches and particularly for microplasmas. A closer look at the basic properties of each plasma source is required.

Table 2 shows the electron temperature (T_e) and the gas temperature (T_g) of some of the plasma sources presented in Table 1, when such information is provided or can be estimated from studies with similar experimental conditions. The estimates of the temperatures for the microplasmas of (Shimizu *et al.* 2006; Mariotti *et al.* 2008) are based on parametric studies of essentially the same plasma source by (Mariotti *et al.* 2007; Mariotti 2008; Stauss *et al.* 2010). Similar experimental conditions to the spark of (Tabrizi *et al.* 2009) can be found in (Reinmann *et al.* 1997; Akishev *et al.* 2007), who simulate T_g for sparks in atmospheric pressure N_2 . Given the planar electrode geometry and applied voltage used by (Tabrizi *et al.* 2009), the reduced electric field is estimated to be about 120 Td, where $1 \text{ Td} = 3 \text{ V}/\text{cm}/\text{torr}$. Using BOLSIG+, a code for the numerical solution of the Boltzmann equation for electrons in weakly ionized gases (Hagelaar *et al.* 2005), it can be calculated that the mean electron energy for such a reduced electric field in argon is 7.16 eV, which we associate here with $T_e \sim 80000 \text{ K}$. (Chen *et al.* 2002) measure T_g and T_e for the same mw torch used in (Chen *et al.* 2003). For the dc arc of (Chen *et al.* 2007), we refer to (Reiche *et al.* 2001), who measure the temperatures of a similar dc arc in argon at 1 atm.

Table 1: Energy cost of incorporating each atom into the nanostructure $\epsilon_{atom} = P / \dot{m}$ using different plasma sources at atmospheric pressure, where P is the power coupled into the plasma and \dot{m} is the mass production rate. In all cases, argon at 1 atm is the carrier gas, and no external substrate heating is used. Quantities marked by (*) have been calculated here based on data given in the listed references.

Source	Nanomaterial	P [W]	Max. \dot{m} [$\mu\text{g}/\text{s}$]	Min. ϵ_{atom} [eV]	References
microplasma	Si nanocrystals	35	0.017	600000*	(Nozaki <i>et al.</i> 2007; Mariotti <i>et al.</i> 2010)
microplasma	MoO_3 nanosheets	31	1*	42000*	(Mariotti <i>et al.</i> 2008)
microplasma	WO_3 nanoparticles	20	35*	1400*	(Shimizu <i>et al.</i> 2006)
spark	Au nanoparticles	1.5*	2*	1500*	(Tabrizi <i>et al.</i> 2009)
mw torch	Graphene	250	33	1000*	(Dato <i>et al.</i> 2008)
mw torch	Carbon nanotubes	400	7	7200*	(Chen <i>et al.</i> 2003)
dc arc	Ag nanoparticles	120*	3	50000*	(Chen <i>et al.</i> 2007)

Table 2: Gas temperature (T_g) and electron temperature (T_e) of some of the plasma sources presented in Table 1. Quantities marked by (*) have been calculated here based on data given in the listed references.

Source	Min. ε_{atom} [eV]	Max. T_g [K]	Max. T_e [K]	References
microplasma	42000*	~2000*	~10000*	(Mariotti <i>et al.</i> 2007; Mariotti 2008; Mariotti <i>et al.</i> 2008; Stauss <i>et al.</i> 2010)
microplasma	1400*	~1000	~50000*	(Shimizu <i>et al.</i> 2006; Mariotti <i>et al.</i> 2007; Mariotti 2008; Stauss <i>et al.</i> 2010)
spark	1500*	~10000	~80000*	(Reinmann <i>et al.</i> 1997; Akishev <i>et al.</i> 2007; Tabrizi <i>et al.</i> 2009)
mw torch	7200*	3000	20000	(Chen <i>et al.</i> 2002; Chen <i>et al.</i> 2003)
dc arc	50000*	8000	12000	(Reiche <i>et al.</i> 2001; Chen <i>et al.</i> 2007)

From Table 2, we see that there is no correlation between gas temperature and energy cost. High energy costs of about 50 keV/atom are obtained at both $T_g = 2000$ K and 8000 K. Low energy costs of about 1 keV/atom are obtained at both $T_g = 1000$ K and 10000 K. On the other hand, the energy cost decreases with increasing electron temperature. The lowest costs are obtained when $T_e = 50000$ K and 80000 K, which is significant if we consider electron impact processes in argon, the carrier gas for all of the experiments discussed above. Figure 1(a) shows the fractional power loss of electron energy to elastic, excitation, and ionization in argon, calculated using BOLSIG+. Processes useful for nanomaterials synthesis such as excitation and ionization consume over 50% of the energy if $T_e > 25000$ K, and ε_{atom} decreases accordingly, as shown in Figure 1(b).

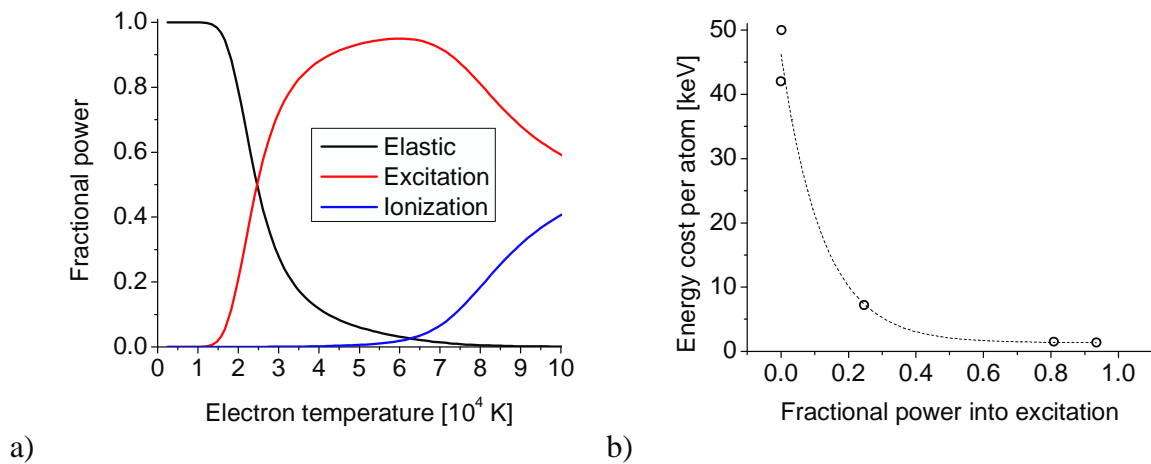


Figure 1: (a) Fractional power transfer into different electron impact processes in argon as a function of the electron temperature. (b) The energy cost per atom for nanofabrication of the plasma sources from Table 2 as a function of the fractional power consumption of electron impact excitation.

Thus, it appears that increasing the electron temperature decreases the energy cost per atom incorporated into the nanomaterial, thus improving nanofabrication efficiency. For mw torches, this is accomplished by increasing the power or introducing aerosol particles into the input gas flow, as demonstrated by (Chen *et al.* 2002), who obtained up to $T_e = 55000$ K. Decreasing the dimensions of microplasmas simultaneously decreases T_g and increases T_e , as shown by (Mariotti 2008), who measured up to $T_e = 14$ eV. For the spark discharge, T_e has been simulated to initiate at high values of ~ 10 eV before decreasing rapidly down to ~ 1 eV (Simek *et al.* 1998; Iza *et al.* 2009), as shown in Figure 2. In the next section, spark discharges with potentially higher average electron energies will be discussed.

Efficient nanofabrication using nanosecond discharges

Table 2 demonstrated that spark discharges have among the lowest energy costs and are therefore already among the most efficient plasma sources for nanofabrication, despite the fact that the electron temperature decreases significantly during spark formation. It follows that ε_{atom} can be decreased further by generating electrons efficiently while T_e is high and then switching off the applied field to avoid inefficiency when T_e is low. In other words, we should shorten the spark duration. Decreasing the duration of pulsed discharges has been demonstrated to increase the average electron temperature (Iza *et al.* 2009). The spark from (Tabrizi *et al.* 2009) shown in Table 1 is $\sim 1 \mu s$ in duration, and therefore it follows that nanosecond-duration discharges have the potential to improve the benchmark for nanofabrication efficiency. In addition, the repetition frequency of such discharges should be made high to achieve high growth rates and to accumulate reactive species over many cycles. We will now present several types of highly repetitive nanosecond discharges that are particularly promising for nanomaterials synthesis.

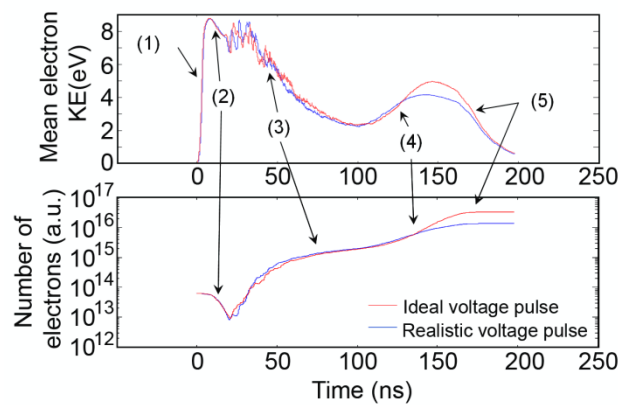


Figure 2: Typical temporal evolution of the electron temperature for a pulsed nanosecond discharge. Reprinted with permission from (Iza *et al.* 2009). According to the caption of the corresponding figure from (Iza *et al.* 2009): (1) Avalanche of seed electrons that remain from the previous pulse. (2) Loss of energetic electrons to the anode. (3) Quasi-neutral plasma formation, confinement of low energy electrons. (4) New avalanches initiated by secondary electrons. (5) Pulse end.

Transient spark discharges

By properly designing a dc discharge circuit, “transient spark” discharges of 100-ns duration can be generated at repetition frequencies of several kHz (Machala *et al.* 2008). The physics of transient sparks has been well studied (Marode 1975; Machala *et al.* 2006; Marode *et al.* 2009), which could facilitate the optimization of their application to nanomaterials synthesis. One engineering advantage of the transient spark for nanofabrication is the simplicity of the generator, as it only requires a dc power supply and passive circuit elements.

Nanosecond repetitively pulsed (NRP) glow discharges

Nanosecond repetitively pulsed (NRP) discharges are generated through the application of high-voltage nanosecond-duration (~ 10 ns) pulses at high pulse repetition frequencies (PRF) of about 10-100 kHz and were originally conceived to generate glow discharges in atmospheric pressure air at low volumetric power (Nagulapally *et al.* 2000; Kruger *et al.* 2002; Packan 2003). The NRP glow discharge is capable of high ionization efficiency and control of the glow-to-arc transition without ballast resistors or dielectric barriers, thus motivating a number of investigations of its basic properties (Starikovskaia *et al.* 2001; Stark *et al.* 2001; Macheret *et al.* 2002; Walsh *et al.* 2006; Adamovich *et al.* 2009;

Pai *et al.* 2009; Bourdon *et al.* 2010). NRP glows can exist **over** a wide range of conditions (Pai *et al.* 2010b) and may be particularly useful for nanomaterials that must be synthesized at low gas temperature.

Nanosecond repetitively pulsed (NRP) spark discharges

The NRP spark discharge is about one order of magnitude more energetic than the NRP glow and can be generated over a wider range of conditions (Shao *et al.* 2006; Naidis 2008; Pai *et al.* 2010a). NRP spark discharges **in atmospheric pressure air** generate high densities of active species such as electronically excited N₂ and atomic oxygen, as summarized in Table 3. In particular, up to 50% of O₂ in air is dissociated into atomic oxygen. Furthermore, the lifetime of atomic oxygen is quite long, such that its minimum density is $2 \times 10^{17} \text{ cm}^{-3}$ (Stancu *et al.* 2009; Stancu *et al.* 2010b). The controlled production of atomic oxygen in NRP sparks **in air** may be useful for tailoring metal oxide nanostructures (Cvelbar *et al.* 2008).

Table 3: Measured densities and lifetimes of active species in NRP spark discharges **in air at atmospheric pressure. Quantities marked by (*) have been calculated here based on data given in the listed references.**

Species	Carrier gas	Max. density [cm^{-3}]	1/e lifetime [ns]	Max. fraction of N ₂ or O ₂	Reference
N ₂ (A)	N ₂	2×10^{15}	600	0.0004*	(Stancu <i>et al.</i> 2010a)
N ₂ (A)	Air	5×10^{14}	<100	0.0001*	(Stancu <i>et al.</i> 2010a)
N ₂ (B)	Air	5×10^{16}	5	0.01*	(Stancu <i>et al.</i> 2010b)
N ₂ (C)	Air	6.1×10^{15}	2	0.002*	(Stancu <i>et al.</i> 2010b)
O	Air	10^{18}	25000	0.5	(Stancu <i>et al.</i> 2009; Stancu <i>et al.</i> 2010b)

Metastable nanomaterials using fast heating and cooling in nanosecond spark discharges

Nanosecond spark discharges **in air at atmospheric pressure** produce sharp thermal spikes, and it is interesting to consider how this property could be exploited, considering the role of thermal processes in plasma nanofabrication (Teo *et al.* 2004; Denysenko *et al.* 2009; Mangolini *et al.* 2009; Wolter *et al.* 2010). **Generally speaking, non-equilibrium thermodynamic conditions favor the formation of non-equilibrium material states. For example, a UHF microplasma very similar to that of (Mariotti *et al.* 2008) has also been used to generate carbon connections between Ag nanoparticles (Levchenko *et al.* 2009). Thermal spikes may facilitate the formation of nanomaterials in metastable material phases (Komatsu 2007). Indeed, carbon-encapsulated metal nanoparticles have been generated recently using spark discharges of millisecond duration (Byeon *et al.* 2010).**

Heating at nanosecond time scales or shorter is typically achieved by the use of lasers (Lorazo *et al.* 2006) and has already been used to synthesize nanomaterials (Geohegan *et al.* 1998). However, it would not be as practical to scale focused lasers to large areas or volumes for industrial applications as it would be for nanosecond discharges arranged in arrays. Here, we discuss the ultrafast heating and cooling of NRP spark discharges as an example of what may be possible under the broader category of nanosecond discharges.

Gas *heating rates of up to 10^{11} K/s*

Figure 3 shows time-resolved measurements of the gas temperature for an NRP spark discharge **in air at atmospheric pressure preheated to 1000 K**, taken from measurements presented in (Pai *et al.* 2010a). **In only about 10 ns**, the temperature rises **from a baseline**

temperature of 1500 K up to 3500 K. The gas heating rate of 10^{11} K/s is the fastest that has been reported for electrical discharges, to the author's best knowledge.

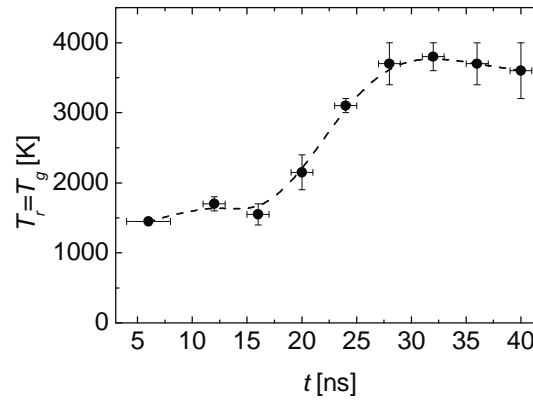


Figure 3: Gas temperature as a function of time for an NRP spark discharge in air at atmospheric pressure preheated to 1000 K, inferred from measured emission spectra of the N₂ (C-B) 0-0 band. Taken from measurements presented in (Pai *et al.* 2010a).

Although only the heating of the gas by NRP sparks has been studied up to now, we can estimate the corresponding heating rate of a nanoparticle, based on a model of heat transfer between a single-wall carbon nanotube (SWCNT) and the surrounding gas (Louchev *et al.* 2004):

$$1) \quad Mc \frac{dT}{dt} = Ah(T_g - T)$$

where h is the heat transfer coefficient, M is the mass of the nanotube, c is its heat capacity, T is its temperature, A is its surface area, and T_g is the gas temperature. Let us consider that $M = mN$, where m is the mass of each carbon atom, and N is the number of carbon atoms in the nanotube. Likewise, $A = aN$, where a is the specific area of each atom in the tube wall. Then the heating rate of the nanotube can be expressed as:

$$2) \quad \frac{dT}{dt} = \frac{ah}{mC}(T_g - T)$$

For heat transfer between the ambient gas and a SWCNT, (Louchev *et al.* 2004) evaluated the heat transfer coefficient:

$$3) \quad h = \frac{3}{2} \alpha Q k_B$$

where $Q = p/(2\pi m k_B T_g)^{1/2}$ is the flux of particles colliding on the SWCNT (p is the gas pressure), k_B is Boltzmann's constant, and α is the accommodation factor for correctly determining collisional energy transfer. (Louchev *et al.* 2004) use $\alpha = 1/3$ to fit their theoretical calculations with molecular dynamics simulations, and the same is done here. Assuming $m = 12$ g/mol for carbon, $p = 1$ atm, and $\alpha = 1/3$, we obtain $h = 7000$ W/m²/K from Equation (3). The heat capacity of a SWCNT at 300 K is 600 J/kg/K (Hone *et al.* 2002), and given that $C \propto T$ (Benedict *et al.* 1996), we take $C = 3000$ J/kg/K at $T = 1500$ K. Thus,

assuming $a = 2.62 \times 10^{-20} \text{ m}^2$ (Louchev *et al.* 2004), $m = 12 \text{ g/mol}$ for carbon, $T = 1500 \text{ K}$, and $T_g = 2500 \text{ K}$, Equation (2) yields $dT/dt = 3 \times 10^9 \text{ K/s}$.

Thus, a nanoparticle could be heated at a rate up to $\sim 10^9 \text{ K/s}$ due to kinetic energy transfer from the gas, which itself is heated by the nanosecond spark discharge. It should be noted that this estimate neglects surface processes such as recombination, chemical reactions, adsorption, desorption, and ion bombardment that also contribute to the heat flux (Denysenko *et al.* 2009; Mangolini *et al.* 2009).

Gas cooling rates of at least 10^7 K/s

The minimum cooling rate of NRP spark discharges in air at atmospheric pressure can be deduced from Figure 3 to be at least 10^7 K/s , based on the fact that the gas temperature returns to 1500 K after a period of $1/\text{PRF} = 33 \text{ } \mu\text{s}$. (Grisch *et al.* 2009) measure 500 K at $\sim 100 \text{ ns}$ after the pulse for a nanosecond discharge under different conditions but at about the same energy per pulse as (Pai *et al.* 2010a), indicating that cooling could even occur at the 100-ns timescale.

In their work on carbon-encapsulated metal nanoparticles, (Byeon *et al.* 2010) report that cooling rates of less than 1400 K/s lead to spheroidization of the nanoparticles, whereas a cooling rate of 2900 K/s causes tube-like graphitization. NRP spark discharges cool at a rate that is least four orders of magnitude faster than the millisecond sparks of (Byeon *et al.* 2010), which may lead to the formation of nanomaterials much further from the equilibrium state of the material than those generated using spark discharges of longer duration.

Outlook

In conclusion, nanosecond discharges at atmospheric pressure possess several basic properties that could be very useful for nanofabrication: high electron temperature, and fast gas heating and cooling rates. These characteristics could be exploited for highly efficient synthesis and for the production of metastable nanomaterials. Among atmospheric pressure plasmas, microplasmas and nanosecond discharges are capable of generating the highest electron temperatures and could complement each other to provide maximum design flexibility for efficient nanofabrication. For example, nanosecond discharges can be employed when confined geometries are disadvantageous.

Finally, it is important to point out that the potential applications for nanosecond discharges in materials engineering are not limited to nanomaterials. The low energy cost per atom for synthesis may be generally true, because high electron temperature is a fundamental characteristic of these discharges. Indeed, nanosecond DBDs have already been used to improve the hydrophilic properties of polymer thin films at relatively high efficiency (Walsh *et al.* 2007; Zhang *et al.* 2010). Also, the crystallization of amorphous Si thin films using plasma-induced thermal annealing at the millisecond time scale has been developed as a practical alternative to laser thermal annealing, albeit at much slower rates of heat transfer (Higashi *et al.* 2006). However, as mentioned previously, NRP spark discharges are capable of heating and cooling on much shorter time scales that may be competitive with some laser annealing techniques.

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References

- Adamovich, I. V., M. Nishihara, I. Choi, M. Uddi and W. R. Lempert (2009). "Energy coupling to the plasma in repetitive nanosecond pulse discharges." Physics of Plasmas **16**(11).
- Akishev, Y. S., G. I. Aponin, M. E. Grushin, V. B. Karal'nik, A. E. Monich, M. V. Pan'kin and N. I. Trushkin (2007). "Development of a spark sustained by charging the stray capacitance of the external circuit in atmospheric-pressure nitrogen." Plasma Physics Reports **33**(7): 584-601.
- Benedict, L. X., S. G. Louie and M. L. Cohen (1996). "Heat capacity of carbon nanotubes." Solid State Communications **100**(3): 177-180.
- Bourdon, A., Z. Bonaventura and S. Celestin (2010). "Influence of the pre-ionization background and simulation of the optical emission of a streamer discharge in preheated air at atmospheric pressure between two point electrodes." Plasma Sources Science & Technology **19**(3).
- Byeon, J. H. and J. W. Kim (2010). "Production of carbonaceous nanostructures from a silver-carbon ambient spark." Applied Physics Letters **96**(15).
- Chen, C. K., W. L. Perry, H. F. Xu, Y. B. Jiang and J. Phillips (2003). "Plasma torch production of macroscopic carbon nanotube structures." Carbon **41**(13): 2555-2560.
- Chen, C. K. and J. Phillips (2002). "Impact of aerosol particles on the structure of an atmospheric pressure microwave plasma afterglow." Journal of Physics D-Applied Physics **35**(10): 998-1009.
- Chen, J. H., G. H. Lu, L. Y. Zhu and R. C. Flagan (2007). "A simple and versatile mini-arc plasma source for nanocrystal synthesis." Journal of Nanoparticle Research **9**(2): 203-213.
- Cvelbar, U., K. Ostrikov and M. Mozetic (2008). "Reactive oxygen plasma-enabled synthesis of nanostructured CdO: tailoring nanostructures through plasma-surface interactions." Nanotechnology **19**(40): 7.
- Dato, A., V. Radmilovic, Z. H. Lee, J. Phillips and M. Frenklach (2008). "Substrate-free gas-phase synthesis of graphene sheets." Nano Letters **8**(7): 2012-2016.
- Denysenko, I. and K. Ostrikov (2009). "Plasma heating effects in catalyzed growth of carbon nanofibres." Journal of Physics D-Applied Physics **42**(1).
- Geohegan, D. B., A. A. Puretzky, G. Duscher and S. J. Pennycook (1998). "Time-resolved imaging of gas phase nanoparticle synthesis by laser ablation." Applied Physics Letters **72**(23): 2987-2989.
- Gonzalez-Aguilar, J., M. Moreno and L. Fulcheri (2007). "Carbon nanostructures production by gas-phase plasma processes at atmospheric pressure." Journal of Physics D-Applied Physics **40**(8): 2361-2374.
- Grisch, F., G. A. Grandin, D. Messina and B. Attal-Tretout (2009). "Laser-based measurements of gas-phase chemistry in non-equilibrium pulsed nanosecond discharges." Comptes Rendus Mecanique **337**(6-7): 504-516.
- Hagelaar, G. J. M. and L. C. Pitchford (2005). "Solving the Boltzmann equation to obtain electron transport coefficients and rate coefficients for fluid models." Plasma Sources Science & Technology **14**(4): 722-733.

- Higashi, S., H. Kaku, T. Okada, H. Murakami and S. Miyazaki (2006). "Crystallization of Si in millisecond time domain induced by thermal plasma jet irradiation." Japanese Journal of Applied Physics Part 1-Regular Papers Brief Communications & Review Papers **45**(5B): 4313-4320.
- Hone, J., M. C. Llaguno, M. J. Biercuk, A. T. Johnson, B. Batlogg, Z. Benes and J. E. Fischer (2002). "Thermal properties of carbon nanotubes and nanotube-based materials." Applied Physics a-Materials Science & Processing **74**(3): 339-343.
- Iza, F., J. L. Walsh and M. G. Kong (2009). "From Submicrosecond- to Nano second-Pulsed Atmospheric-Pressure Plasmas." IEEE Transactions on Plasma Science **37**(7): 1289-1296.
- Komatsu, S. (2007). "New type of BN nanoparticles and films prepared by synergetic deposition processes using laser and plasma: the nanostructures, properties and growth mechanisms." Journal of Physics D-Applied Physics **40**(8): 2320-2340.
- Kortshagen, U. (2009). "Nonthermal plasma synthesis of semiconductor nanocrystals." Journal of Physics D-Applied Physics **42**(11).
- Kruger, C. H., C. O. Laux, L. Yu, D. M. Packan and L. Pierrot (2002). "Nonequilibrium discharges in air and nitrogen plasmas at atmospheric pressure." Pure and Applied Chemistry **74**(3): 337-347.
- Levchenko, I., K. Ostrikov and D. Mariotti (2009). "The production of self-organized carbon connections between Ag nanoparticles using atmospheric microplasma synthesis." Carbon **47**(1): 344-347.
- Lorazo, P., L. J. Lewis and M. Meunier (2006). "Thermodynamic pathways to melting, ablation, and solidification in absorbing solids under pulsed laser irradiation." Physical Review B **73**(13): 22.
- Louchev, O. A., H. Kanda, A. Rosen and K. Bolton (2004). "Thermal physics in carbon nanotube growth kinetics." Journal of Chemical Physics **121**(1): 446-456.
- Machala, Z., M. Janda, K. Hensel, I. Jedlovsky, L. Lestinska, V. Foltin, V. Martisovits and M. Morvova (2006). Emission spectroscopy of atmospheric pressure plasmas for bio-medical and environmental applications. 19th International Conference on High Resolution Molecular Spectroscopy (PRAHA 2006), Prague, CZECH REPUBLIC, Academic Press Inc Elsevier Science.
- Machala, Z., I. Jedlovsky and V. Martisovits (2008). "DC discharges in atmospheric air and their transitions." Ieee Transactions on Plasma Science **36**(4): 918-919.
- Macheret, S. O., M. N. Shneider and R. B. Miles (2002). "Modeling of air plasma generation by repetitive high-voltage nanosecond pulses." IEEE Transactions on Plasma Science **30**(3): 1301-1314.
- Mangolini, L. and U. Kortshagen (2009). "Selective nanoparticle heating: Another form of nonequilibrium in dusty plasmas." Physical Review E **79**(2).
- Mariotti, D. (2008). "Nonequilibrium and effect of gas mixtures in an atmospheric microplasma." Applied Physics Letters **92**(15).
- Mariotti, D., H. Lindstrom, A. C. Bose and K. Ostrikov (2008). "Monoclinic beta-MoO₃ nanosheets produced by atmospheric microplasma: application to lithium-ion batteries." Nanotechnology **19**(49).
- Mariotti, D. and R. M. Sankaran (2010). "Microplasmas for nanomaterials synthesis." Journal of Physics D-Applied Physics **43**(32).
- Mariotti, D., Y. Shimizu, T. Sasaki and N. Koshizaki (2007). "Gas temperature and electron temperature measurements by emission spectroscopy for an atmospheric microplasma." Journal of Applied Physics **101**(1).

- Marode, E. (1975). "MECHANISM OF SPARK BREAKDOWN IN AIR AT ATMOSPHERIC-PRESSURE BETWEEN A POSITIVE POINT AND A PLANE .1. EXPERIMENTAL - NATURE OF STREAMER TRACK." Journal of Applied Physics **46**(5): 2005-2015.
- Marode, E., D. Djermoune, P. Dessante, C. Deniset, P. Segur, F. Bastien, A. Bourdon and C. Laux (2009). "Physics and applications of atmospheric non-thermal air plasma with reference to environment." Plasma Physics and Controlled Fusion **51**(12).
- Nagulapally, M., G. V. Candler, C. O. Laux, L. Yu, D. M. Packan, C. H. Kruger, R. Stark and K. H. Schoenbach (2000). 31st AIAA Plasmadynamics and Lasers Conference. Denver, Colorado. **AIAA Paper 2000-2417**.
- Naidis, G. V. (2008). "Simulation of spark discharges in high-pressure air sustained by repetitive high-voltage nanosecond pulses." Journal of Physics D-Applied Physics **41**(23): 8.
- Nozaki, T. and K. Okazaki (2008). "Carbon nanotube synthesis pressure glow discharge: A review." Plasma Processes and Polymers **5**(4): 301-321.
- Nozaki, T., K. Sasaki, T. Ogino, D. Asahi and K. Okazaki (2007). "Microplasma synthesis of tunable photoluminescent silicon nanocrystals." Nanotechnology **18**(23).
- Ostrikov, K. (2005). "Colloquium: Reactive plasmas as a versatile nanofabrication tool." Reviews of Modern Physics **77**(2): 489-511.
- Ostrikov, K. and A. B. Murphy (2007). "Plasma-aided nanofabrication: where is the cutting edge?" Journal of Physics D-Applied Physics **40**(8): 2223-2241.
- Packan, D. M. (2003). Stanford University. **Ph.D. Thesis**.
- Pai, D. Z., D. A. Lacoste and C. O. Laux (2010a). "Nanosecond repetitively pulsed discharges in air at atmospheric pressure – the spark regime." Plasma Sources Science & Technology **19**(6): 065015.
- Pai, D. Z., D. A. Lacoste and C. O. Laux (2010b). "Transitions between corona, glow, and spark regimes of nanosecond repetitively pulsed discharges in air at atmospheric pressure." Journal of Applied Physics **107**(9): 093303.
- Pai, D. Z., G. D. Stancu, D. A. Lacoste and C. O. Laux (2009). "Nanosecond repetitively pulsed discharges in air at atmospheric pressure – the glow regime." Plasma Sources Science & Technology **18**: 045030.
- Reiche, J., F. Konemann, W. Mende and M. Kock (2001). "Diagnostics of discharge modes of a free-burning low-current argon arc." Journal of Physics D-Applied Physics **34**(21): 3177-3184.
- Reinmann, R. and M. Akram (1997). "Temporal investigation of a fast spark discharge in chemically inert gases." Journal of Physics D-Applied Physics **30**(7): 1125-1134.
- Shao, T., G. S. Sun, P. Yan, J. Wang, W. Q. Yuan, Y. H. Sun and S. C. Zhang (2006). "An experimental investigation of repetitive nanosecond-pulse breakdown in air." Journal of Physics D-Applied Physics **39**(10): 2192-2197.
- Shimizu, Y., A. C. Bose, D. Mariotti, T. Sasaki, K. Kirihara, T. Suzuki, K. Terashima and N. Koshizaki (2006). "Reactive evaporation of metal wire and microdeposition of metal oxide using atmospheric pressure reactive microplasma jet." Japanese Journal of Applied Physics Part 1-Regular Papers Brief Communications & Review Papers **45**(10B): 8228-8234.
- Simek, M., V. Babicky, M. Clupek, S. DeBenedictis, G. Dilecce and P. Sunka (1998). "Excitation of N-2(C (3)Pi(u)) and NO(A (2)Sigma(+)) states in a pulsed positive corona discharge in N-2, N-2-O-2 and N-2-NO mixtures." Journal of Physics D-Applied Physics **31**(19): 2591-2602.

- Stancu, G. D., M. Janda, F. Kaddouri, D. A. Lacoste and C. O. Laux (2010a). "Time-resolved CRDS measurements of the $N_2(A^3\Sigma^+u)$ density produced by nanosecond discharges in atmospheric pressure nitrogen and air." J. Phys. Chem. A **114**(1).
- Stancu, G. D., F. Kaddouri, D. A. Lacoste and C. O. Laux (2009). Investigations of the rapid plasma chemistry induced by nanosecond discharges in atmospheric pressure air using advanced optical diagnostics. 40th AIAA Plasmadynamics and Lasers Conference. San Antonio. **3593**.
- Stancu, G. D., F. Kaddouri, D. A. Lacoste and C. O. Laux (2010b). "Atmospheric pressure plasma diagnostic by OES, CRDS and TALIF." J. Phys. D.: Appl. Phys. **43**(12): 124002.
- Starikovskaia, S. M., N. B. Anikin, S. V. Pancheshnyi, D. V. Zatsepin and A. Y. Starikovskii (2001). "Pulsed breakdown at high overvoltage: development, propagation and energy branching." Plasma Sources Science & Technology **10**(2): 344-355.
- Stark, R. H. and K. H. Schoenbach (2001). "Electron heating in atmospheric pressure glow discharges." Journal of Applied Physics **89**(7): 3568-3572.
- Stauss, S., Y. Imanishi, H. Miyazoe and K. Terashima (2010). "High rate deposition of ZnO thin films by a small-scale inductively coupled argon plasma generated in open air." Journal of Physics D-Applied Physics **43**(15).
- Tabrizi, N. S., M. Ullmann, V. A. Vons, U. Lafont and A. Schmidt-Ott (2009). "Generation of nanoparticles by spark discharge." Journal of Nanoparticle Research **11**(2): 315-332.
- Teo, K. B. K., D. B. Hash, R. G. Lacerda, N. L. Rupesinghe, M. S. Bell, S. H. Dalal, D. Bose, T. R. Govindan, B. A. Cruden, M. Chhowalla, G. A. J. Amaratunga, J. M. Meyyappan and W. I. Milne (2004). "The significance of plasma heating in carbon nanotube and nanofiber growth." Nano Letters **4**(5): 921-926.
- Walsh, J. L. and M. G. Kong (2007). "10 ns pulsed atmospheric air plasma for uniform treatment of polymeric surfaces." Applied Physics Letters **91**(25).
- Walsh, J. L., J. J. Shi and M. G. Kong (2006). "Submicrosecond pulsed atmospheric glow discharges sustained without dielectric barriers at kilohertz frequencies." Applied Physics Letters **89**(16).
- Wolter, M., I. Levchenko, H. Kersten and K. Ostrikov (2010). "Hydrogen in plasma-nanofabrication: Selective control of nanostructure heating and passivation." Applied Physics Letters **96**(13).
- Zhang, C., T. Shao, K. H. Long, Y. Yu, J. Wang, D. D. Zhang, P. Yan and Y. X. Zhou (2010). "Surface Treatment of Polyethylene Terephthalate Films Using DBD Excited by Repetitive Unipolar Nanosecond Pulses in Air at Atmospheric Pressure." Ieee Transactions on Plasma Science **38**(6): 1517-1526.
- Zheng, J., R. Yang, L. Xie, J. L. Qu, Y. Liu and X. G. Li (2010). "Plasma-Assisted Approaches in Inorganic Nanostructure Fabrication." Advanced Materials **22**(13): 1451-1473.