Nanomaterials synthesis in air at atmospheric pressure using nanosecond repetitively pulsed spark discharges

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Atmospheric pressure microplasmas have attracted much interest for nanofabrication in low-temperature non-equilibrium conditions (Mariotti *et al.* 2009). Scaling up plasma-based nanofabrication processes to the industrial scale is the primary motivation for improving their efficiency. 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 and show that increasing the electron temperature (T_e) decreases ε_{atom}, thus improving nanofabrication efficiency. Along with microplasmas, spark discharges of microsecond duration have among the lowest ε_{atom}, despite the fact that T_e 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. Decreasing the duration of pulsed discharges has been demonstrated to increase the average electron temperature (Iza *et al.* 2009). Therefore it follows that nanosecond-duration discharges have the potential to serve as interesting alternatives to microplasmas for efficient nanofabrication.

Among nanosecond discharges, nanosecond repetitively pulsed (NRP) spark discharges are particularly intriguing for nanofabrication because they are applied at high pulse repetition frequency (PRF), enabling the accumulation of active species such as atomic oxygen (Stancu *et al.* 2010). Furthermore, NRP spark discharges heat the gas at a rate of 10^{11} K/s, which is the fastest that has been reported for electrical discharges, to the authors' best knowledge (Pai *et al.* 2010). The minimum cooling rate of NRP spark discharges in air at atmospheric pressure can be deduced 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/PRF = 33 µs. Generally speaking, non-equilibrium thermodynamic conditions favor the formation of non-equilibrium material states. Indeed, carbon-encapsulated metal nanoparticles have been generated recently using spark discharges of millisecond duration (Byeon *et al.* 2010), who 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.

Finally, we demonstrate the first use of NRP spark discharges in air at atmospheric pressure for synthesizing metal-based nanostructures. The discharge is generated across a gap (1-2 mm) formed by two metal electrodes in a vertical pin-pin or pin-plane configuration. Positive-polarity high-voltage (7-13 kV) pulses of 40-ns duration are applied across the electrodes at PRF = 30 kHz. The fabricated nanostructures include Mo nanoflakes and nanowalls, as well as Ti nanodots.

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.

References

Byeon, J. H. and J. W. Kim (2010). Applied Physics Letters **96**(15).
Iza, F., J. L. Walsh and M. G. Kong (2009). IEEE Transactions on Plasma Science **37**(7): 1289-1296.
Mariotti, D., A. C. Bose and K. Ostrikov (2009). IEEE Transactions on Plasma Science **37**(6): 1027-1033.
Pai, D. Z., D. A. Lacoste and C. O. Laux (2010). Plasma Sources Science & Technology **19**(6): 065015.
Stancu, G. D., F. Kaddouri, D. A. Lacoste and C. O. Laux (2010). J. Phys. D.: Appl. Phys. **43**(12): 124002.

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