Progress report: Direct injection of liquids into low-pressure plasmas

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Abstract. While laboratory based plasmas are always in contact with solid surfaces (often vacuum chambers) they have historically been formed in gas environments. In more recent times, the use of plasmas has grown to include plasma contact with liquids including biological items. Inevitably the plasmas in contact with liquids had been at or near atmospheric pressures. This need not be the case. We have developed a novel method for injecting liquids directly into low-pressure discharges. As such, this technique opens new areas of possible industrial use for plasmas. For example, we have injected inorganic nano-particles into argon plasma by suspending them in hexane (or ethanol) as a high vapor pressure liquid carrier. As a result, we believe that metals, dielectrics, superconductors, aromatics, proteins, viruses, etc. could all potentially be injected into low-pressure plasma environments using this technique. The resulting films indicate the ability to synthesize nano-structured composites. Here we examine some of the basic phenomenon that are observed both experimentally and theoretically.

1. Introduction

Liquids have been used for processing in other systems but not in the same manner as is being reported here. For example, Senateur, et al. [1] show direct liquid injection into an MOCVD tool. In that technique the liquid (solvent, solute) is injected onto a heated, porous, moving tape in an area of the tool that is relatively cool. The tape, with liquid, is moved toward a warmer (~300 °C) portion of the tool, causing the solvent to evaporate. A 'vector' gas is introduced in a position along the path of travel such that the evaporating solvent sweep always from the process area. The tape, now containing only the solute, reaches the process area wherein solvent evaporates and is transported to the substrate. Such techniques have been used to grow YBa2Cu3O7 superconductors. Plasma spray methods are also well known for introducing liquids (solvent, solute) into plasmas. However these operate at much higher pressure and much higher neutral temperatures. See for example Ref [2]. Finally M Coppins has reported the production of liquid droplets in ‘dusty’ plasmas. None of these exhibit our desired situation: Low pressure, Low neutral temperature, Plasma interactions, resulting in thin film deposition from fragile or non-volatile precursors.

2. Experimental efforts

We have build a simple apparatus that combines a automotive fuel injector with traditional low pressure, low temperature plasmas, see figure 1[3]. This allows us to inject a wide range of materials directly into a discharge, including solvents with non-volatile or fragile precursors. Examples might include solids and DNA or viruses. This technique is inexpensive to setup and we find that we can
control the liquid insertion to a reasonable level. This new technique also opens new areas of plasma science research. For example we find that the plasma reacts in fascinating ways to the pressure wave induced by the injection process. This is seen in the emission from the discharge as shown Figure 2.

We have used the system to inject various species. Typical of those are hexane and ethanol. In figures 3 and 4 we show the deposition as a function of time. Specifically we have used injector pulse widths of 1.3 and 2 ms. At 1 atmosphere backing pressure and 1 Hz pulses on the injector, these times correspond to flow rates of 70 and 110 µL/min. In addition to the liquid injection we also have 20 SCCM of Ar as a buffer gas, 10 W or rf (13.56 MHz) power and heated the chamber to 60 °C. The pumping system was set to achieve ~ 400 mTorr.

**Figure 1.** System layout for the liquid injection tool. The heart of the system is an automotive fuel injector, allowing the input of various liquid mixtures.

**Figure 2.** Time sequence of change in emission during N$_2$ injection into Ar plasma. Change in emission is determined via background subtraction. Here black represents a decrease in emission, white represents an increase and gray is no change. Time is given relative to initiation of injection.
Such process steps result in films such as those shown in figure 5. Figure 6 shows a film produced from Hexane with 2 nm Fe nano-particles. Here the Fe represents \( \sim 4.3\% \) of the film by volume. Process conditions are as in Figure 3, with the 1.3 ms injector pulse widths. Deposition times are \( \sim 10 \) minutes.

**Figure 3.** Typical film thicknesses for hexane injections.

**Figure 4.** Typical film thicknesses for ethanol injections.
Figure 5. Typical films for a) hexane b) ethanol injections.

Figure 6. Typical films for hexane with 2 nm Fe nano-particles.

3. Modeling efforts
Models of the time evolution of the injected liquid have been developed based on the processes shown in figure 7[3]. Without a plasma, the model indicates that the time required for the droplet to fully evaporate is a function of the background pressure, initial (wall) temperature, the number of droplets inserted simultaneously and initial size, see figure 8.

It is evident that the evaporation falls has two distinct temporal periods. The first period is set by evaporation of the solvent, along with a rapid cooling, see figure 9. For example both water and benzene rapidly reach freezing temperatures and the liquid evaporation process becomes a sublimation process.
Figure 7. Parameters considered in the model of the evolution of liquid droplets in a low-pressure, low-temperature plasma discharge. Note that we have not yet included surface chemical reactions in the model.

Figure 8. Time sequence of 50 µm n-hexane droplet injected into 1 and 10 mTorr Ar. Plasma greatly speeds this evaporation rate.
Figure 9. Droplet temperature as a function of time. We note that certain droplets will rapidly fall below the freezing point, e.g. benzene at 278 °C and water at 273 °C. Once this happens the evaporation is via sublimation.

Adding a plasma brings additional heat to the surface through ion impact and electron-ion recombination. This can result in a significant increase in the evaporation – and a corresponding decrease in the total evaporation time. (This time is the duration it takes to go from an initial size of 50 µm to 100 nm.) Figure 10 shows the influence of a plasma on a hexane droplet. At low densities the plasma has very little impact. At very high plasma densities, the evaporation is almost instantaneous. At more typical densities, e.g. \( \sim 10^{16} \) m\(^{-3} \), the temperature of the electrons has a major influence. The electron temperature impacts the energy flux to the surface via the floating potential of the droplet in the plasma. The higher the temperature the higher the potential and hence the higher the impact energy of the ions. At very high densities, the recombination of the ions and electrons on the surface drives the evaporation. Here the energy flux is set by the overall flux of ions and electrons to the surface.
In addition to single component droplets, we have also examined two component droplets. In figure 11 we examine the temperature on a multi-component droplet as a function of time. Here there are a number of stages. In the first stage, the droplet temperature decreases rapidly as the initial evaporation occurs. It then reaches a stage in which the heat loss due to evaporation is balanced by plasma heating. When all of the hexane has evaporated, the droplet begins to heat up. It eventually reaches a steady state temperature that is set by a balance between radiative cooling and plasma heating.
When both the solute and the solvent have non-zero vapor pressures the droplet responds in a slightly different fashion. Figure 12 and 13 show the predicted droplet radius and droplet temperature as functions of time for a mixture of 1% ferrocene in hexane. First it observed that the droplet undergoes the typical rapid drop in radius as it also undergoes a rapid drop in temperature. It then reaches a quasi steady state temperature regime set by evaporative cooling (hexane) balancing plasma heating. When the hexane is exhausted, there is a brief period during which the droplet temperature increases rapidly, while the droplet does not shrink in size. After this period the droplet will have reached a new balance temperature, again set by a balance of evaporative cooling and plasma heating, with the evaporation now consisting of ferrocene.

**Figure 12.** Modeled droplet radius for hexane + 1% ferrocene in Ar.

**Figure 13.** Modeled droplet temperature for hexane + 1% ferrocene in Ar.
4. Conclusions
We have shown that it is possible to directly inject liquids (solvent and solute) into low-pressure plasmas and use them to produce films that are not possible through other methods. Our models indicated that the droplet undergo significant temperature and radial shifts. There is an initial temperature drop due to evaporative cooling followed by steady state temperatures set by energy balances. In some cases the droplet even freeze. The nature of the energy input, plasma vs. neutral bombardment, plays a major role in determining the lifetime of the droplet. Under just neutral bombardment, droplets can take many seconds to evaporate. Moderate plasma densities significantly reduce the evaporation times to a few tenths of second or less.

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