the Bell Jar
Vacuum Technique and Related Topics for the Educator & Amateur Investigator

Notes from the Vacuum Shack **No. 10 September 2020**

In this issue:

- Thin Film Deposition Using Essential Oils

This has been a busy month with a variety of things. As a result I'm deferring a few planned items to next month. However, I hope that the musings in the following article will generate some interest.

Thin Films with Pleasant Smelling Stuff

One of the earliest applications that got amateurs involved in vacuum was the aluminizing of homemade telescope mirrors by evaporation. With regard to thin film plasma processing by amateurs, this has generally focused on sputtering. The equipment is fairly simple: a negative target electrode and a high voltage DC power supply. Argon is generally used as the process gas if one is producing a pure metal film. Reactive sputtering can be accomplished by admitting oxygen or nitrogen along with the argon. Ion milling (sputter etching) just involves reversing the power supply polarity. This also applies to the educational vacuum trainers that have been marketed. More complex educational systems generally use small 13.56 MHz RF generators with matching networks. These will also incorporate more complex sources, e.g. magnetron guns. Systems like the PPTS-1A from MKS also had a provision for simple reactive sputtering. Additionally, the RF systems can be used to deposit insulating films.

A recently developed trainer (based on the MKS VTS-1B and the TSS VPAL-A) is the VAPPOR (Vacuum and Plasma Process Operator Trainer) that was developed by the Northeast Advanced Technology Education Center (NEATEC), a program of SUNY Polytechnic. This trainer can demonstrate DC, 60 Hz and RF, the last using a 27 MHz CB radio with matching network. This can produce plasmas in parallel plate and coaxial electrode geometries.

Plasma enhanced chemical vapor deposition (PECVD) is another major class of thin film processing. However, the chemicals used in most of the PECVD processes tend to be rather nasty to work with in less than a properly outfitted lab or industrial facility.

My eyes were opened a bit when I read a brief section in Chapter 11 of *Plasma Science and Technology for Emerging Economies – An AAAPT Experience*. (This book was reviewed in the January 2020 issue of this newsletter.) The chapter, *Plasma Polymerization: Electronics and Biomedical Application* [1] covers the use of the usual hydrocarbon monomers (e.g. ethane, methane and cyclohexane) and fluorocarbons and silicon-containing monomers (silane, TEOS, HMDSO and the like). However, the section ends with a brief note on "Plasma polymerization from natural precursors." To quote:

> Plasma polymerization from natural precursors has received significant interest in modern times. Natural precursors have wide range of chemical compositions, for example the tea tree oil has 16 chemical components. Fabrication of plasma polymer films from various essential oils like lavender oil, tea tree oil, orange oil, and their components has been reported. The essential oils can easily evaporate at room temperature, which make these precursors compatible to PECVD process. The plasma polymer films fabricated from essential oil at low power are generally transparent. The chemical structure analysis by FTIR shows that irrespective of the starting precursor material, the FTIR spectra of deposited plasma polymers possess similar chemical features.
>
> Plasma-polymerized films from essential oils have been studied for their application in the biological field, e.g., as coatings for medical implants and in organic electronics, e.g., as dielectrics.

The only experience I've had with essential oils are the little bottles of liquid that my wife has around the house with some sort of wicking things sticking out of the bottle. In small doses they smell good. Essential oils are readily available and are fairly inexpensive.

After a bit of searching I found a number of readily available papers that might be good starting points for amateur experimentation as well as for use in educational settings. These involve both low pressure and atmospheric pressure PECVD. A good overview is provided in the 2016 review paper on cold plasma processing by Dey *et al.* [2]. The following sections present some ideas for further experimentation. I've selected references that are readily available on the web.

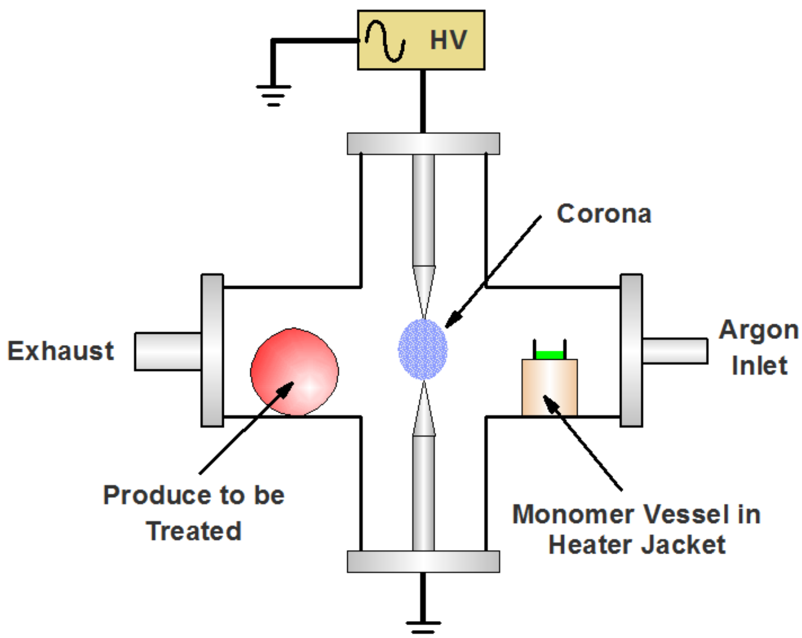
Preservation of Produce Using Cold Plasma Generated Films

Sulmer A. Fernández-Gutierrez *et al*. [3] describe a process using a corona discharge with vanillin as a precursor to deposit a protective polymer film on produce. The abstract states:

> Active packaging of fruits and vegetables uses films that absorb molecules from or contribute molecules to the produce. The pilot application developed in this paper has resulted in the deposition of film to apples. A prospective application relates to replacing hot wax that is expensive and that lowers the textural quality of the apple. This was the early motivation of this paper. Moreover, the focus of this paper will be mostly on the reactor design and film evaluation. The cold-plasma zone was obtained by increasing the voltage on a needle-to-needle electrode structure until the electric field in the feed material (argon + monomer) was sufficiently high to yield electron avalanches and self-propagating streamers. The "corona onset criterion" was used to design the cold-plasma reactor. The apple was placed in a treatment chamber downstream from the activation zone (cold-plasma zone). Selected physical properties of the film were measured. Environmental scanning electron microscopy and Fourier transform infrared studies of

> samples were also performed to determine the presence of the film. Electromagnetic modeling was applied to the design of the cold-plasma reactor, and those results are presented in this paper.

A diagram of the reactor is shown in the figure. While the device is shown in a large Pyrex tee, there should be no reason why a simpler chamber couldn't be used, even one made from plastic. The monomer is evaporated with a heater jacket and is conducted through the corona by means of flowing argon. The author notes that a dielectric barrier discharge (DBD) configuration could also be used. The monomer used was vanillin. In the reactor, the monomer container is heated to a temperature (47 °C) that is adequate for sublimation at atmospheric pressure. Further details are in the paper.



Deposition of Plasma Thin Films from Cineole

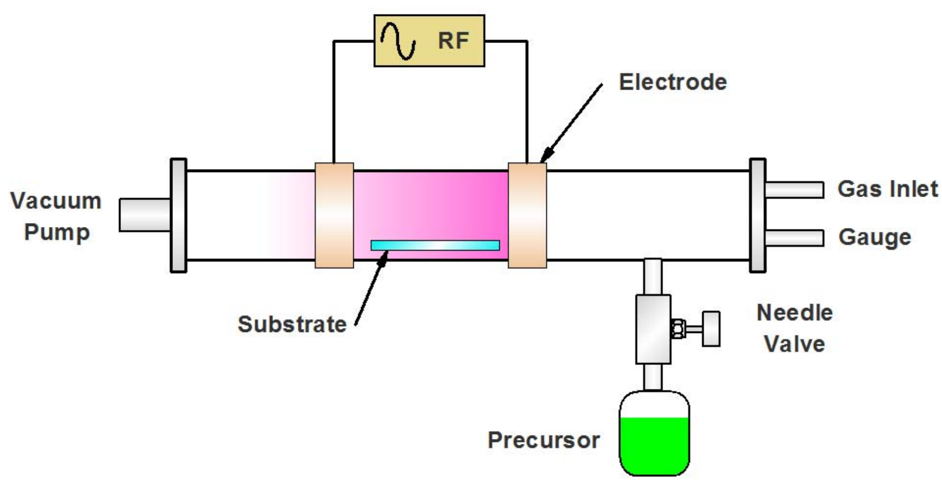
Easton *et al*. [4] describe a low pressure PECVD process for the deposition of a thin film using 1,8-Cineole as the precursor. 1,8-Cineole, or Eucalyptol, is a saturated monoterpene and it is major component of Eucalyptus oil. From the abstract:

> The development of organic polymer thin-films is critical for the progress of many fields including organic electronics and biomedical coatings. This paper describes the fabrication of an organic polymer thin film produced from 1,8-cineole via radio frequency plasma polymerisation. A deposition rate of 55 nm/min was obtained under the polymerisation conditions employed. Infrared spectroscopic analysis demonstrated that some functional groups observed in the monomer were retained after the polymerisation process, while new functional groups were introduced.

The refractive index and extinction coefficient were estimated to be 1.543 (at 500 nm) and 0.001 (at 500 nm) respectively. The polymers were shown to be optically transparent. AFM images of the polymer established a very smooth and uniform surface with average roughness of 0.39 nm. Water contact angle data demonstrated that the surface was stable while in contact with water.

Below is a diagram of the apparatus, based on the illustration in the paper. The copper electrodes are spaced at a distance of 11 cm. While not noted in the paper, I believe that this is the same chamber that is referenced in several other papers and is 50 mm in diameter. The monomer is contained in a vial that is connected to the chamber 12 cm upstream of the right electrode. Excitation is by a 13.56 MHz 25 watt power supply. I don't see any particular reason why useful results couldn't be obtained by using a pulsed low frequency (ca. 20-100 kHz) power supply of the type used for the excitation of atmospheric pressure cold plasma discharges. These are relatively simple and inexpensive to construct. The authors describe the use of several types of substrate, selected based on the type of analysis to be used. Glass slides were one of the options and these are readily available as microscope slides.

In operation, the monomer vial is first put under vacuum before the substrate is placed in the chamber. The isolation valve is then closed. Then, with the substrate in place, the chamber is pumped while being flushed with argon. Finally, the argon is turned off and the monomer vapor released while the plasma is ignited. The pressure is controlled by the amount that the isolation needle valve is opened. Process pressure was on the order of 33 Pa (248 Torr).



A related thesis by Easton [5] is also worth exploring. Here the monomer is *Lavandula angustifolia* essential oil (LAEO). Also, Jacob *et al.* [6] where linalool is used as the precursor.

I would suggest that anyone wishing to replicate or build on this work use a simple dedicated system with an inexpensive pump and adequate exhaust ventilation.

Dielectric Barrier Discharges for PECVD

DBD discharges (and plasma jets) are used without precursors for surface treatments (e.g. enhancement of wetting) and for killing bacteria and spores. These topics alone would be a useful avenue for amateurs to explore. Basic wetting studies are straightforward. For the latter simply get a bacteria science kit with pre-poured agar in Petri dishes. Grow some colonies and see how efficiently you can kill them off with the cold plasma.

DBDs are commonly used for thin film deposition. There are a number of papers that are related to the PECVD of essential oils. Getnet *et al.* [7] discuss the use of carvacrol, a natural oil that is extracted from oregano, to produce biocidal polymer films on stainless steel implants.

The precursor can be delivered to the parallel DBD electrodes from the side but the more efficient method is to deliver the vapor to the center of one of the electrodes. This is the approach used in the reference. The powered electrode is uncovered and the ground electrode has the dielectric plate. The substrate is placed on the dielectric covered lower electrode.

The Atmospheric Pressure Plasma Jet (APPJ) and PECVD

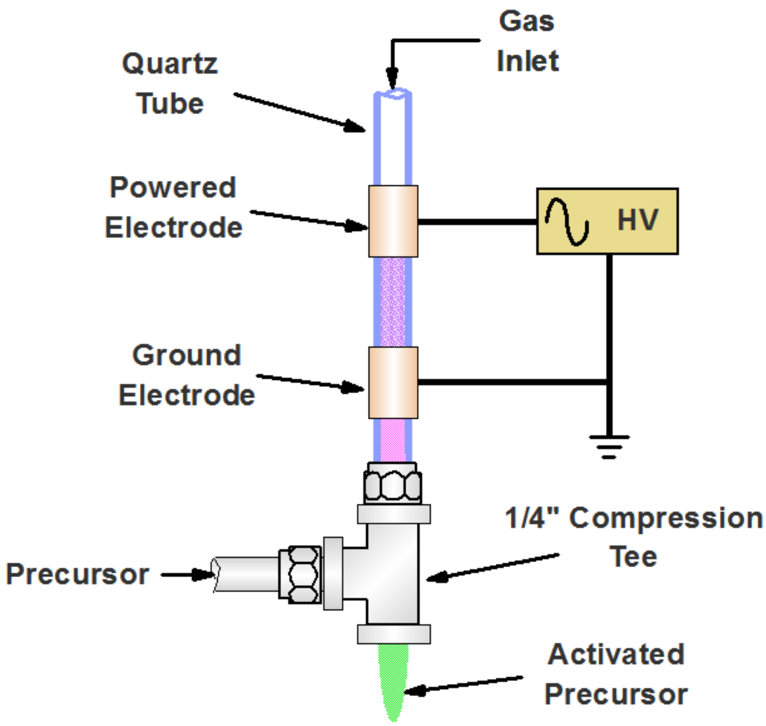
The APPJ as described in a couple of recent issues of this newsletter can be used “as is” for a variety of applications. These include adhesion and wettability improvement of polymers and sterilization. Another application is in the area of film deposition by PECVD. This is implemented by the introduction of a material into the plume of the plasma jet. The material may be introduced as a vapor or as an aerosol.

Commercial APPJ devices such as those made by Surfx and PlasmaTreat have been used to deposit wear resistant coatings on aircraft windows using octamethylcyclotetrasiloxane (OMCTS) and tetramethylcyclotetrasiloxane (TMCTS). The passivation of metal surfaces has been done using aqueous phosphoric acid or chromic acid as the passivating agents. Acrylic acid is a relatively safe (but corrosive) and inexpensive monomer that is often used with cold plasma devices (DBD and APPJ) for the deposition of polymer films.

While I keep looking, I have not yet come across a paper that describes the use of an APPJ for PECVD of essential oils. I’m by no means an organic chemist but it would seem that films could be deposited using an APPJ along with an essential oil such as described in the preceding sections.

The illustration on the next page shows an implementation that I am working on. This consists of my quartz capillary device as previously described with a ¼” compression tee affixed to the open end. Since the quartz tube is a bit undersized (6 mm OD x 3 mm ID), I built the lower end of the tube up with a couple of turns of copper tape. This allowed the plastic ferrule to just slip over the copper. The tape used for this and for the electrodes is 10 mm wide. The spacing between the electrodes is about 15 mm.

The precursor is admitted through the side connection and the plasma activated precursor exits through the end port. I removed the threaded portion on the lower port of the tee to expose more of the afterglow plume. Depending upon what precursor is used, the material can be introduced as a vapor or aerosol.



References

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Articles of Possible Interest in *Vacuum Technology & Coating* Magazine

May 2015
Impediments to Good Vacuum: Permeation, outgassing and trapped gas sources
The pumping of a vacuum system is not as simple as removing x liters of gas from a chamber whose volume is x. Instead, there are a multitude of sources within the system that create a larger gas load as well as gases that might be hiding in various nooks and crannies that simply take time to deal with.

September 2012
A Visit to the Vacuum Gauge Graveyard
Antique and obsolete gauges can still tell us interesting things about the workings of the vacuum environment.

Articles may be accessed at http://vtcmag.com/. Scroll to the bottom of the page to the back issue selection box. Look for my columns and you can probably find other articles of interest in each issue.

That’s it for this month.

Steve