ADVANTAGES OF TCO VIA ULTRASONIC SPRAY UNDER ATMOSPHERIC CONDITIONS

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ABSTRACT

1. Define TCO

Transparent Conductive Oxides (TCOs) are metal oxide layers, often doped, that are used on optical surfaces such as photovoltaic panels, architectural and transportation glass, and interactive devices such as touch panels. Modern ovens are made with glass covered in a TCO layer that makes the outside surface safe to touch. Electrochromic mirrors and windows use TCOs as coated electrodes. In this application Fluorine doped tin oxide is typically paired with electrically active organic gel to make the electrochromatic effect. TCOs are also used to defrost windows in super-markets, cars and on airplanes. A current is passed through the coating, which inhibits the formation of frost on the glass, keeping the view free of obstructions. Indium Tin Oxide (ITO) replaced the tin oxide used on airplane glass in WWII. Doped ITO has dominated the market throughout the past decade because of its lower resistance and capability of defrosting a larger area with a lower voltage. Chemical inertness and high transparency are main factors that contribute to the selection of the TCO. Definitively, the most demanding application is solar panels where a TCO layer replaces the gridlines of electron "collectors" which block the solar photons and are not as electrically efficient as TCO's.

Materials used depend on the ultimate goal of the coating. Some applications require higher temperature resistance, some require lower emissivity and still others focus more on bandgap. Traditionally Indium Tin Oxide solves many of these challenges, though there is a limited supply world-wide. Fluorine doped versions offer excellent durability and lower cost than ITO. Additionally, there currently exists a major effort to maximize Aluminum-doped Zinc Oxide (AZO) as these costs are even more attractive.

2. Define Early Deposition Techniques: Sputtering and Spray Pyrolysis

Different deposition methods vary for TCO coatings. Deposition techniques are dependent on the type of application in which they are being utilized. Spray pyrolysis was the first deposition technique to be used, but in the past decade was replaced by sputtering. This trend is shifting back to spray pyrolysis due to rising costs and limited efficiency associated with sputtering.

In sputtering, a target containing the metallic material is bombarded from the back with ions. These ions create a cascade of collisions in the target. When the correct energy is used relative to the

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target thickness, atoms of the metal on the opposite side can be freed of the surface binding energy in transmission. The freed atoms exit the surface at many angles and are not stable thermodynamically except when under vacuum conditions. In a vacuum, all surfaces will develop a coating from the freed material as will the substrates, which are typically glass or silicon wafers. By definition, the process is very inefficient in terms of transfer efficiency, but also very costly to operate due to the strong vacuum conditions required, typically between 0.1 to 10 millitorr, and due to the extreme voltages that are used. High voltages are required to generate the plasma typically used to bombard the targets.

From the Greek for "Fire" and "Separating", pyrolysis is the method of using heat, often intense (between 300 to 700 C), to cause a permanent change in a material. In spray pyrolysis, there are a number of stages and manipulations. The first stage, and easiest, is to force the carrier (solvent or water) out of the sprayed droplets before the droplets make contact with the substrate. The second method can be understood as running the substrate hot enough that a chemical reaction takes place in the material after it makes contact with a substrate of sufficient temperature. A third manipulation would be to run the substrate hot enough that the material sprayed both dries in the air before contact and undergoes a chemical reaction before hitting the substrate. The final and typically the hottest spray pyrolysis process would be defined as dry chemical reactions that happen in the plume before contact with the substrate and further chemical reactions occurring once the sprayed material is in contact with the substrate.

All of the above processes are affected by two key factors: variable droplet size and flow rate as it pertains to plume velocity during atomization. If the droplets start at significantly different sizes, it will take more energy to be at the same reaction point for a large droplet as opposed to a smaller droplet within a given point in the stream. This causes such a great chemical imbalance that in some cases the chemistry may be ruined by the high heat. Another negative effect of various droplet sizes is that large droplets will hit the substrates wet, without having enough time to start the necessary alterations. If, however, the droplets are all of a uniform size, then a larger percentage of the sample, if not all, can be expected to be in a given state of humidity or chemical reaction.

Control of the kinetic energy during atomization allows for more versatile and effective results. Often, atomization via various methods such as dual-fluid or "air atomizers" creates a plume of very high velocities that are related to droplet size and to flow rate. A process engineer in pyrolysis would prefer the ability to independently control the velocity of both the liquid and air shaping. They may prefer a much longer plume state before contacting to the substrate, allowing a more thorough chemical reaction with a lower substrate temperature. Certain methods of atomization do not create this type of variable control and may even prevent a successful coating chemistry.

Of the above noted deposition techniques, sputtering and spray pyrolysis, neither one is highly ideal in all applications for optimal results.

3. Define Ultrasonic

a. On the high-tech end of atomization technologies is the ultrasonic method. High frequency standing waves are introduced in nozzles with piezo-electric transducers at rates of 25,000 to 250,000 vibrations per second. These vibrations in the nozzle body set up standing waves in the liquid. When these wave heights are increased just enough to cause instability in the liquid, droplets fall off the site of each wave top which are mathematically definable by combining the work of Lord Rayleigh[3] with the work of Lang[2] "and as made commercially viable by Dr. Harvey Berger in the mid 1970s:

$\boldsymbol{\lambda_L = ((8*\pi*\theta)/(\rho*f^2))^{1/3}}$ (2) And $\boldsymbol{D_{N,\,0.5} = .34*\lambda_L}$ (3)

Where:
π = pi
θ = Surface Tension
ρ =Density
f = Frequency of Nozzle
$D_{N,\,0.5}$ = Number Median Diameter of Droplet size
λ_L = Wavelength in the liquid

HIGH FREQUENCY ATOMIZATION OF CAPILLARY WAVES

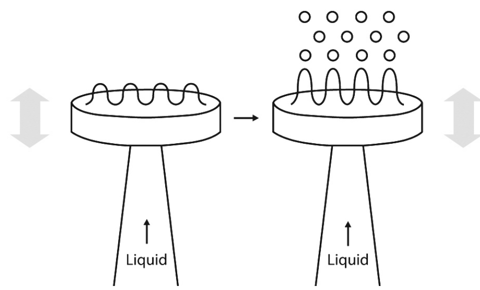


Figure 1 - Illustration of wave formation and atomization

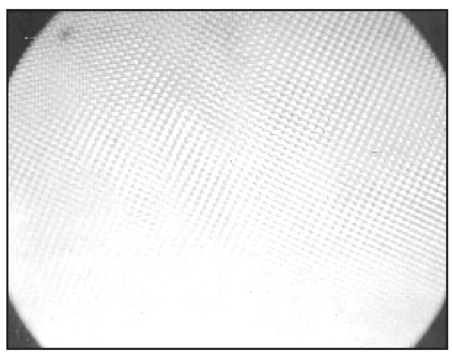


Figure 2 - Droplets forming on nozzle tip

b. The result of the technology is the droplets produced are of a uniform size, created with little to no kinetic energy during atomization. The ultrasonic nozzle is a device which acts in a manner similar to an ultrasonic bath and exposes the material to vibrations helping to disperse the material before atomizing them. This both prevents clogging of the nozzle and breaks agglomerations in a manner similar to that of using ultrasonics to break down kidney stones or to clean teeth.

COMPARISON OF
MEDIAN DRIOP SIZE

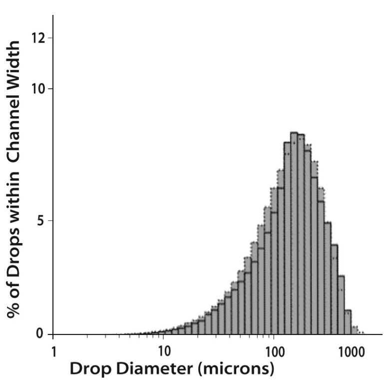


Figure 3a - Diameter of droplets from hydraulic nozzle

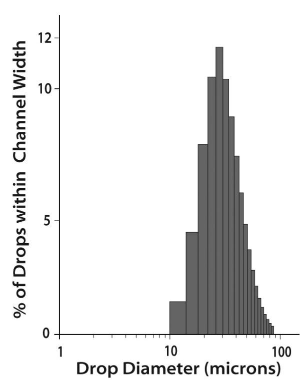


Figure 3b - Diameter of droplets from ultrasonic nozzle (Sono-Tek Corp.)

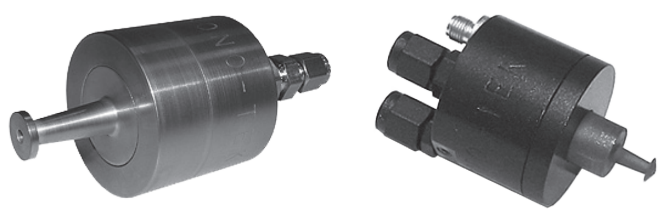
c. Ultrasonic nozzles produce a soft, low velocity spray resulting in minimal overspray. When low velocity gas is used to shape the spray plumes of ultrasonic atomizers, the highest transfer efficiencies of expensive materials are possible. The following are inherent conditions consistent with the use of ultrasonic nozzles:

- The droplets atomized are of a significantly consistent size relative to other methods.
- The soft spray is easily shaped into a uniform pattern with controllable gas.
- The technology allows for a large turn down ratio of flow rates, maximizing the flexibility of an atomizing platform.
- The large orifice and ultrasonics make it possible to atomize high-solid materials without any concern for clogging.
- The nozzle's titanium construction makes it highly inert to many solvents resulting in high reliability and long life.

4. Summarize Process Challenges

The first process challenge that requires engineering upgrade is the high temperature required. Pure radiation from the substrate largely depends on the size of the substrate. Since the construction of the ultrasonic device has a temperature limit, cooling is required to ensure the transducers do not depolarize.

A much more difficult challenge is that the process chemistry does not lend itself well to standard metallic alloys. Hydrochloric acid is widely used in the process. Sono-Tek Corporation has developed a pair of platforms that are survivable in these more challenging applications: the Gold Series Ultrasonic Nozzle and the Cobalt Series Ultrasonic Nozzle. These platforms have been extensively tested under harsh acidic conditions and found to exceed the survivability of standard titanium by 20x and 2000x respectively.



5. Summarize Advantages

Because ultrasonic atomization creates droplets of a uniform size, the chemistry being deployed has a substantially higher chance of being at a uniform chemical state at any given point in the process.

Because the process plume velocity can be controlled independently of atomization, the droplet size or flow rate can be finely tuned by the process engineer to have the appropriate "plume duration" in order to achieve the ideal chemical state before contacting the substrate. This is an advantage that is not available with most atomization methods.

The technology of ultrasonic atomization spraying and coating, when combined with advanced nozzles materials that resist acidic corrosion, has been proven to meet the demanding requirements of the TCO spray pyrolysis application better than other available methods.

Notes

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[2] Lang, 1962

[3] Rayleigh, "Theory of Sound", 1898