

## SVC Topics

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## PVD Processes: Gas Evaporation & Nanoparticles

 $\mathbf{N}^{\mathrm{anoparticles}}$  are particles having only a few to a few thousand atoms in a cluster that is less than a micron in size. Other names for such particles are "ultrafine particles," "soot," "smoke" and, in early ion plating work, "black sooty crap." In vacuum coating processing, nanoparticles are formed by the gas-phase nucleation of atoms or molecules either from a vaporization source (PVD) or from the decomposition of a chemical vapor precursor, either in a hot gas (CVD) or in a plasma (PECVD). In plasma etching, nanoparticles can form from the vaporized etch products.

The particle density necessary for initiating gas phase nucleation can come either from a high-density vapor source or from a combination of condensable species and a highparticle-density, non-condensing gaseous environment ("gas evaporator"). Initial nucleation occurs when multiple particles collide at once and the energy of condensation is carried off by non-condensing particles. As the particle grows in size, individual atoms can condense on the particle because the condensation energy is insufficient to cause vaporization from the particle. In some cases, the condensing atoms can react with a reactive gaseous species to form nanoparticles of compound material, such as metal oxides. The noncondensing particles then must remove the heat of reaction, as well as that of condensation.

The nanoparticles can deposit on surfaces to form a very low-density coating. Pfund produced "zinc black" infrared adsorbing films by this method in 1933. "Gold black" particle films are now used for radiation adsorption from low-intensity sources, such as stars. Nanoparticles

of many pure metals are very reactive and will form a thin oxide on the surface when first exposed to air. With this oxide film, they are stable, but if disturbed in air, they may spontaneously ignite and burn. Commercially prepared nanoparticles of reactive materials are collected and stored in vacuum or under an inert gas.1

In gas evaporation, the vapors are formed

by thermal evaporation or arc vaporization in a few Torr gas pressure. Often, the gas is a combination of a high-mass inert gas such as argon, and a low-mass inert gas such as helium. The high-mass gas allows effective momentum transfer, and the low-mass gas allows easy removal of heat by conduction. Metal-alloy nanoparticles can be formed by co-evaporation. Because many compound materials vaporize as molecules, nanoparticles of these compounds can be formed by gas evaporation with no gas phase reaction. The figure shows a Transmission Electron Microscope (TEM) micrograph of nanoparticles of RbCl.2

Carbon nanoparticles may be in the form of solid clusters or hollow spheres ("buckministerfullerenes") or tubes ("nanotubes"), which are really carbon molecules. The spheres are formed by arc vaporization of carbon electrodes in a gas. The solid clusters of the carbon nanoparticles are dissolved in boiling benzene or tolulene followed by vacuum drying, leaving the carbon spheres. Anywhere from three percent to 30 percent of the carbon nanoparticles may be spheres,



Transmission electron microscope (TEM) micrograph of RbCl nanoparticles.

depending on the conditions of preparation.

Plasmas in contact with walls assume a positive potential with respect to the wall, because electrons are lost to the wall faster than ions. In plasmas, the nanoparticles that are formed have a negative charge with respect to the plasma for the same reason. The negative nanoparticles are repulsed by the walls and are suspended in the plasma. The particles in the plasma tend to migrate to the edge of the plasma and grow with time. The particles will remain suspended in the plasma until the plasma is extinguished, then they will deposit on surfaces. In PVD processing, as long as there is a negative potential on the substrate/fixture, the nanoparticles will not settle on the substrate surface.

In regions where there is no plasma generation, such as in the throat of the high-vacuum pump where pressure is low, the negatively charged nanoparticles will be attracted to ground metal surfaces. When using a turbomolecular pump with a screen over the inlet, for example, the nanoparticles will accumulate on the screen and decrease the conductance into the pump. Nanoparticles that get into the high-vacuum pump can cause maintenance problems, particularly with turbopumps and cryopumps.

When using a plasma process that generates nanoparticles, it is usually best to extinguish the plasma by cutting off the gas flow and reducing pressure while the voltage is still present. This allows more of the particles to be swept into the pumping system and fewer particles to deposit on the walls and surfaces in the vacuum chamber.

Nanoparticles can form when vaporizing any material, but some processes generate more nanoparticles than others. Nanoparticles of carbon are extensively formed in PVD processing when reactively depositing metal carbides or carbonitrides using acetylene ( $C_2H_2$ ) or methane ( $CH_4$ ) for the source of carbon. Sulfur nanoparticles are formed when using hydrogen sulfide ( $H_2S$ ) in the quasireactive sputter deposition of sulfide materials.

One way to minimize the problem of nanoparticles entering the highvacuum pump is to place a multilayer metal screen or mesh filter in the pump inlet. Such a filter will reduce the coductance to the pump and, if this is a concern, the filter can be placed on an actuation mechanism such as that used for valves. By removing the filter, the conductance can be high during pump-down and the filter can be put in place when nanoparticle generation is occurring. During reactive deposition, limiting the conductance is desired to reduce the gas flow through the system.

The buildup of soot on the surfaces of the vacuum system will affect the pump-down behavior of the vacuum system. In particular, water vapor and other vapors will be retained by the low-density particle layer. The system should therefore be cleaned more often than would normally be done if nanoparticles were not being generated.

Cleaning Techniques

Removing (cleaning) the nanoparticles is aided by poor adhesion, low density and the high surface area of the deposits. Care must be taken in removing metal soots, because the deposits may be pyrophoric and catch on fire if disturbed in air while dry. Wet cleaning techniques may be best. To remove the soot, the surface may be wiped using a water-wetted cloth followed by a wipe-down with anhydrous alcohol. For removing carbon soot from difficult-to-reach regions, the surfaces can be cleaned by immersing in boiling 30-percent hydrogen peroxide—the  $H_2O_2$  will oxidize the carbon. *In situ* cleaning of carbon soot from the system can be done using an oxygen plasma.

The production of nanoparticles (ultrafine particles) can be a useful

technological process. The deposition of soot in the vacuum system is undesirable from a vacuum technology standpoint. PRSF

References

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