Ultrafine particles are generally defined as particles whose size range is between 1 and 100 nanometers (10 – 1000 Å) (PM1.0) while fine particles are in the range of 100-2500 nanometers (PM2.5) [1]. Particles finer than PM2.5 are inhalable into deep recesses of the lungs and may be a source of health problems (nanotoxicology). Nanoparticles are often defined as particles having at least one dimension less than 100 nanometers thus may include structures such as nanotubes and nanowires, which may be longer than 100 nanometers [2]. Ultrafine and nano- particles have a very high surface to volume ratio and thus may have quite different properties than the bulk material [3]. Ultrafine and nano- particle research is currently an area of intense scientific interest due to a wide variety of potential applications in biomedical, optical and electronic fields. Nanoparticles also have been the subject of a Crichton sci-fi book [4].

Ultrafine particles may be generated by nucleation in a fluid and some of the earliest studies were of the optical properties of colloidal suspensions of ultrafine particles [4a]. Michael Faraday led the way with his paper “Experimental relations of gold (and other metals) to light” which was presented to the Royal Society in 1856 [5]. Later the optical studies were continued and applications were enumerated [6]. Ultrafine particles may also be generated by gas phase nucleation and are ubiquitous in nature being called “smoke” in their airborne state and “soot” when condensed on surfaces.

Ultrafine particles may be generated in reduced pressure gases (vacuum e.g. 10 Torr or greater) by gas phase nucleation (“gas evaporation”).

Formation by Evaporation into a Gaseous Ambient (1-100 Torr)
Preparation of ultrafine particles by gas phase nucleation in vacuum goes back at least to Pfund (1930) and Burger and Cittert (1930) who studied the optical properties of the deposits of ultrafine particles [7-9]. The studies of the optical properties of vacuum-ormed ultrafine particles has been periodically revisited ever since [10-12]. In 1963 Uyeda et al. used “gas evaporation” to prepare ultrafine particles [13,14] and studied the unique properties of ultrafine particles by electron microscopy and electron diffraction. Others began theoretical studies [15]. Vaporization in vacuum was studied using resistance and inductive heating evaporation, plasma jets, and electric arcs. By the late 1970s the gas evaporation process had been scaled-up to the production of quantities (kilograms) of various materials [16,17]. Ultrafine particles are of interest in powder metallurgy processing by hot isostatic pressing (HIPing), formation of ferrofluidic liquids (invented by NASA in 1963 for weightless environments), and for preparation of electrically conductive pastes (“thick film” slurries).

In general it is found that the size, shape, and crystallinity of the particles are dependent on the vapor flux and the gaseous particle density and species [18,19]. There have been some attempts to increase the out-of-line-of-sight deposition (enhanced coverage) by evaporated films by using gas scattering (“scatter plating”) but this hasn’t worked very well [20].

A problem with the gas phase nucleation process is the coalescence of the particles into “clumps.” One means of avoiding this problem is to evaporate (e-beam) the material into a “good” vacuum (minimal gas phase nucleation) and nucleating the material (“island stage” of nucleation and growth) on the surface of flowing oil. This can produce particles of <10 nm size with a narrow size distribution [21,22]. Thin films of narrow-gap (<0.6 eV) semiconductors should be good selective solar absorbers since they absorb in the solar spectrum (<2 µ) but transmit in the infrared (>2 µ). Unfortunately, semiconductors have high indices of refraction which give high reflectivity from smooth surfaces and thus have poor solar–absorbing efficiency. In order to reduce the solar reflectance of semiconductor films of silicon, germanium and lead sulfide were formed by gas evaporation. The reflectance was reduced to less than 5% but the absorption edge was shifted to an unacceptable degree [23].

Evaporation in reactive gases results in the formation of ultrafine particles of compound materials [24-26]. By going to higher pressures thermal plasmas [27] can be formed by DC arc or rf discharges and used to increase the ultrafine particle formation rate [28]. C60 and C70 particles (fullerene molecules) were first identified in carbon vapor produced by laser ablation of graphite in helium gas [29]. Kroto, Curl and Smalley received the Nobel Prize in Chemistry for their work on the fullerenes.

The particles that are formed by gas phase nucleation may be subsequently ionized and accelerated to high velocities [30]. Such particles are used to study astrophysics questions.

Formation by Vaporization into a Cold Plasma (5-20 mTorr)
In the early work on ion plating [31,32] Mattox found that ultrafine particles were deposited on the interior walls of the chamber but not on the negatively biased substrate. The particles that formed in the plasma attained a negative charge and were repelled by the negative potential on the substrate. In the case of reactive materials such as titanium, the deposited ultrafine particles were stable when exposed to air, apparently because of a surface oxide. When disturbed the fine particles will “burn.” To quote Mattox [p. 427 (section 8.9.2) in Handbook of Physical Vapor Deposition Processing, Donald M. Mattox, Noyes Publications (1998)]

“In the early work on ion plating, the particles formed in the plasma and deposited on the walls was called ‘black sooty crap’ (BSC) and could be very pyrophobic. One game was to ask an observer to wipe the particles off a window with a paper towel. When the window was wiped, the towel caught fire and a flame front moved over the surface of the chamber.”

With the advent of high rate sputtering the formation of ultrafine particles was noted in the sputtering plasma [33-36]. The particles are suspended in the plasma and grow with time. They tend to be concentrated near the edge of the plasma. Ultrafine particles can be deposited on the substrate during “gas flow sputtering” [37, 38, 48].

Formation by Vaporization into a “good” Vacuum
Atom cluster have been formed by vacuum evaporation through as gas cell to give “clusters” of atoms [39].

In 1972 Toshinori Takagi reported the formation and ionization of atom clusters by expansion from a thermal evaporation source through a “nozzle”[40]. Yamada and Takagi explain the cluster formation as being due to “adiabatic expansion and subsequent cooling to...
supersaturated conditions” [41,42]. The clusters typically contain 200 – 2000 atoms. By ionizing the clusters they may be accelerated under an electric potential. This gives rise to the Ionized Cluster Beam (ICB) deposition technique [43,44]. Postvaporization ionization of clusters in vacuum may be done in several ways [45].

Conclusion

The fabrication and study of ultrafine particles has a long history and has lead to some significant advances. As the applications spread to other applications, the field will continue to advance.

The formation of ultrafine particles can be detrimental to some vacuum coating processes. The deposition of particles in the vacuum system necessitates more frequent cleaning to maintain pump-down goals. If the particles are deposited on a substrate or growing film they may cause “killer” defects in a semiconductor device. Deposition of particles on vacuum pump components such as screens (turbopump) or adsorption surfaces (cryopump) can change their pumping characteristics. Collection of fine particles in pump oil with turn it black though this may not hinder its function (same is true of diesel engines).

The term ultrafine particles is being replaced by the terms nanoparticles or nanoclusters [46] so care should be taken to look at both when doing a literature or patent search.

Note added in proof: In many ways the properties of films/coatings resemble those formed using nanostructural deposition techniques [47]. Nanoparticles embedded in a thin film may also be fabricated by co-deposition [48].

References

History Corner

A Short History of Ultrafine (nano-) Particles Formed in a Vacuum

continued from page 55

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About the Author

Donald M. Mattox

Don served as a meteorologist and Air Weather Officer in the USAF during and after the Korean War. After being discharged from the USAF he obtained an M.S. degree on the G.I. Bill, and went to work for Sandia National Laboratories in 1961. Don retired in 1989 after 28 years as a Member of the Technical Staff and then as a Technical Supervisor. Don was President of the American Vacuum Society (AVS) in 1985. In 1988, the 9th International Congress on Vacuum Metallurgy presented him with an award for “outstanding contributions to metallurgical coating technology for the period 1961-1988” and in 1995 he was the recipient of the AVS Albert Nerken Award for his work on the ion plating process. Don was the Technical Director of the Society of Vacuum Coaters (SVC) from 1989 to 2006. In 2007 Don received the Nathaniel Sugerman Award from the SVC. Don is presently the Technical Editor for the SVC.

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