SVC Topics

Donald M. Mattox, Technical Director • Society of Vacuum Coaters
71 Pinon Hill Place N.E. • Albuquerque, NM 87122
505/856-7188 • FAX: 505/856-6716 • www.svc.org

Plasma Technology: Plasma Chemistry, Etching & Deposition*

Plasma chemistry is important to vacuum coating technology. It is used to deposit coatings directly from a precursor gas(es) or vapor(s) ("plasma deposition") to co-deposit material, along with PVD processes (hybrid deposition) to "activate" reactive gases, and to perform plasma cleaning and stripping. Plasma-based chemical reactions may take place in the gas phase or on a surface in contact with the plasma, or a combination of the two. Examples of the use of plasma chemistry in vacuum coating are: plasma-enhanced chemical vapor deposition (PECVD) of phosphosilicate glass (PSG), deposition of diamond-like carbon (DLC) films, reactive PVD of TiC_xN_y hard coatings, activation of oxygen for plasma cleaning and reactive deposition of oxides, "functionalization" of polymer surfaces, and activation of NF_3 (atomic fluorine) for plasma stripping.

A plasma is a gas that contains enough ions and electrons to be able to conduct a current when a voltage is applied between two electrodes immersed in the plasma.[1] A plasma can be either "cold," where the particle energies are near ambient temperature (1/40 eV at 22°C), such as that found in a fluorescent light, or can be very "hot," such as those studied for atomic fusion, where the particle temperature can approach 104°C. Often the electron temperature and ion temperature differ in a plasma.

An ion may be generated by a high-energy electron striking an atom, ejecting an electron from the atom and leaving an excess of positive charge to create a positive ion:

$$A + e^- \rightarrow A^+ + 2e^-$$

A second electron can be removed, giving a doubly charged positive ion (A^{++}). The primary region in which ions are being created is called the plasma-generation region. The plasma-generation region can occupy the entire region between electrodes, as with rf-generated plasmas,[1] or may be confined to a small portion (cathode dark space) of the interelectrode region, as in DC diode nonmagnetically confined plasmas.[1] The table shows the energy necessary to generate singly charged and doubly charged ions. It is important to note that this energy is released when the ion com-

First Ionization Potentials (eV)

Ar	15.7	0	13.6
Al	6.0	CH_4	14.1
Au	9.8	C_2H_2	11.6
Cl	12.9	C_6H_6	9.6
Cr	6.7	Cl_2	13.2
F	17.3	F_2	17.8
H	13.5	H_2	15.6
He	24.4	HCl	13.8
Hg	10.3	NO	9.5
Na	5.1	N_2O	12.9
Ne	21.4	O_2	12.5

Second Ionization Potentials (eV)

Ar	27.76	Na	47.0
O	34.93	Cr	16.6

Metastable States

Species	Metastable Energy Levels (eV)	
He	19.82	20.61
Ne	16.62	16.71
Ar	11.55	11.72
Kr	9.91	9.99
Xe	8.31	8.44

Cold Plasma Color

Argon—violet	Copper—green
Oxygen—yellow-white	Sodium—yellow
Nitrogen—red-yellow	Mercury—blue-green
Hydrogen—pink	Air—reddish

*Revised Version of Plasma Chemistry in 2000 Guides.

Free Details: Circle 139 on reader service card or visit www.aesf.org

bines with an electron(s). Figure 1 shows the number of ions formed by an electron, with the indicated energy per centimeter of path length, for various gases at 10 mTorr. The most effective electron energy for ionization is about 100 eV. This energy is supplied to the electron by acceleration in an electric field.

Electron collision can also ionize molecular species such as:

$$N_2 + e^- \rightarrow N_2^+ + 2e^-$$

The electron-molecule collision can also fragment the molecular species to form uncharged species (dissociation), such as:

$$O_2 + e^- \rightarrow 2\,O + e^-$$

In the case of oxygen, the oxygen atom will react with an oxygen molecule to form ozone (O_3). Ozone is a very reactive oxygen species. The impact can also result in a charged fragment (dissociative ionization). Negative ions (A^-) can be formed by electron attachment.

An electron-atom collision can also create an excited atom where the electron is not completely removed from the atom. Excitation is often accompanied by de-excitation and the emission of photons at specific wavelengths that appear as characteristic colors of the atoms that have been excited. Excitation and de-excitation of the outermost electrons of the atom will generate a visible spectrum (4100 Å to 7200 Å, or 3.0 eV to 1.7 eV) that gives a color characteristic of the plasma gas. De-excitation of electrons closer to the atom nucleus will cause emission of ultraviolet (UV) radiation and soft X-rays. Some excitation states are stable (metastable states) until collision with another atom or a surface. The table gives some metastable state energies for various atoms. Also shown are some characteristic plasma colors.

If a metastable atom (A*) collides with a different atom (B) whose ionization energy is less than the excitation of A*, then the de-excitation of A* can ionize (or excite) B. This process is called Penning ionization and is common in gas and gas/vapor mixtures. For example:

$$Ar^* \text{ (11.55 eV)} + Cr^o \text{ (ionization energy = 6.7 eV)} \rightarrow Ar^o + Cr^+ + e^-$$

Therefore, the plasma will consist of neutral atoms, excited-radiating species, excited-metastable species, ionized atoms (ions), electrons, ionized molecular fragments (radicals), and "new species." In addition, there will be photon radiation (visible and UV) from the plasma. Many of these species are more chemically reactive than the initial molecular gas species. Therefore, the gas species is said to be "activated" in the plasma. At 1 eV particle energy, the electron will have a velocity about 200 times that of an argon ion. Because electrons are accelerated in an electric field during plasma generation, the electron temperature can be significantly higher than the heavy-particle temperature in some regions of the plasma.

In many cases the plasma may contain a high percentage of neutral particles and is called a "weakly ionized" plasma. In PVD processing, a "weakly ionized" plasma may have a ratio of one ion to 1,000 neutrals. The relative numbers of each species can vary depending on a number of factors, such as type of plasma generation, power input into the plasma, location in the plasma, and gas density. The plasma density can be determined using small-area Langmuir probes, rf attenuation, or rf polarization effects. Outside the plasma-generation region, the plasma is volumetrically neutral (except near surfaces). This means that there are equal numbers of electrons and ions per cubic centimeter.

Ions, as well as electrons, are accelerated by the applied electric field. These high-energy ions can lose their charge by a "charge-exchange" mechanism whereby the high-energy ion can receive an electron from a neutral, creating a low-energy ion and a high-energy neutral. These high-energy neutrals are unaffected by electric or magnetic fields. The energetic ions and neutrals can lose energy by physical collision with neutral gas species ("thermalization"), thereby raising the temperature of the gas.

Chemical reactions in the plasma can either decompose compounds, form new compounds, or begin dissociation of molecular species in the plasma. Chemical reactions (decomposition and synthesis) in plasmas have been studied since about 1800.[2] In many vacuum coating processes, the chemical reactions begin in the plasma and continue at the plasma-surface interface. Chemical reactions may be initiated in the plasma-generation region, where electrons are being accelerated to high energies in electric-field gradients or out of the plasma-generation region ("remote," "downstream," or "afterglow" region), where there is no electric field gradient.

Gaseous-compound production in the plasma can be important in vacuum coating processes. For example, ozone (O_3) is formed by dissociation of the oxygen molecule and the combination of atomic oxygen with molecular oxygen to form ozone. Ozone is a powerful oxidizing agent and is more strongly adsorbed on surfaces than is O_2. Also, SiH_4 can form Si_2H_6, which is more strongly adsorbed on silicon than is SiH_4. Absorption and ion bombardment of the adsorbed species can play an important role in reactive-deposition and plasma-deposition processes.[3]

Organic and inorganic monomers can be polymerized in the plasma and on the surface.[4] If there are reactive gaseous species present, the polymerizing species can react to vary the chemical composition of the polymer. For example, hydrogen-containing siloxaine can be polymerized into an $Si\text{-}O_x\text{-}H_y$ polymer with varying degrees of oxidation.

SUR/FIN® 2001, Booths 637, 736 & 738
Free Details: Circle 140 on reader service card or visit www.aesf.org

Plasma decomposition of chemical-vapor precursors can form ultrafine "nanoparticles" in the plasma. For example, decomposition of acetylene (C_2H_2) forms carbon nanoparticles, and the decomposition of H_2S forms nanoparticles of sulfur. In the plasma, these nanoparticles attain a negative potential with respect to the plasma and are repelled by the walls. This suspends the particles in the plasma, where they grow and are swept into the vacuum-pumping system, sometimes clogging screens.

Plasma-surface interactions are important in vacuum coating processes. Any unbiased surface in contact with a plasma will have a negative potential (generally a few volts) with respect to the plasma, because of the higher mobility of the electrons as compared to the ions. This "sheath potential" will accelerate positive ions from the plasma to bombard the surface. This kinetic energy (a few eV), along with the ionization energy (tens of eV) that is released on neutralization, enhance desorption of and chemical reaction with atomic or molecular species on the surface ("ion scrubbing").

If the surface has a high negative "self-bias" or an applied bias, positive ions can be accelerated to high kinetic energies if the gas pressure (density) is rather low (*i.e.*, little thermalization—up to about 50 mTorr). This high kinetic energy, along with the released ionization energy, can promote dissociation of molecular species and chemical reaction between adsorbed (condensed) species and surface species. This can result in the formation of chemical compounds that either volatilize (plasma etching) or remain on the surface (coating formation - reactive deposition).

In a plasma, there are a number of chemical reactions that take place. Most of these reactions involve the interaction of an energetic electron with an atom or molecule. The plasma, which "activates" reactive gases, is important in reactive deposition processes where the depositing atoms react with the gaseous ambient to form a compound material. When plasma deposition is combined with physical vapor deposition (PVD), the process is called a hybrid deposition process. In PVD technology, the plasma is a source of ions for bombardment of sputtering targets in sputter deposition and bombardment of growing films in ion plating. In arc vapor deposition, the plasma becomes the gaseous current-carrying medium. *P&SF*

References

1. *Glow Discharge Processes*, Brian Chapman, John Wiley (1980).
2. *The Electrochemistry of Gases and Other Dielectrics*, G. Glocker & S.C. Lind, John Wiley (1939).
3. *Handbook of Physical Vapor Deposition (PVD) Processing*, D.M. Mattox, Section 9.5, William Andrew/Noyes Publications (1998).
4. *Plasma Polymerization*, H.K. Yasuda, Academic Press (1985); *Plasma Deposition, Treatment and Etching of Polymers*, edited by R. d'Agnostino, Academic Press (1991).

Courses Offered by SVC at SUR/FIN

- Introduction to PVD Processes
- Sputter Deposition in Manufacturing
- Evaporation as a Deposition Process

To register, contact SVC at 505/856-7188 or visit www.svc.org.