

SVC Topics

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Plasma Chemistry & PVD Processes

A plasma is a gas that contains enough ions and electrons to be able to conduct a current when a voltage is applied to two electrodes immersed in the plasma. Plasmas are found in everyday use in fluorescent lights, sodium vapor lamps and neon signs.

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. The plasma, which "activates" reactive gases, is also important in reactive PVD processes where the depositing atoms react with the gaseous ambient to form a compound material. 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.

If an energetic electron strikes an atom, it can temporarily excite an atomic electron to a higher energy state. This electron will spontaneously return to an unexcited level (deexcitation) and the atom will emit radiation of a specific wavelength that is characteristic of the atom.

Relative ionizability of various gases.

Electrons deexciting from all excited levels will give an emission spectrum characteristic of the atoms involved. Excitation and deexcitation 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 is characteristic of the gas (plasma color). Deexcitation of electrons closer to the atom nucleus will cause emission of ultraviolet (UV) radiation and soft X-rays.

Electrons can also be excited to metastable states (A*) where they will remain without spontaneous deexcitation until they collide with a surface or another atom to which they can release their energy.

Electrons can also be excited to such an energy that they are removed from the atom, leaving a singly charged positive ion, such as:

Hydrogen (pink)

 $A + e^{-} = > A^{+} + 2e^{-}$

A second electron can be removed, giving a doubly charged positive ion. The figure 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. The table gives the energies necessary to excite electrons into various metastable states and to remove the first

First Ionization Potentials			
Ar	15.7 eV	0	13.6 eV
Al	6.0	CH	14.1
Au	9.8	C,Ĥ,	11.6
CI	12.9	CÉHÉ	9.6
Cr	6.7	Cl ₂	13.2
F	17.3	F	17.8
Н	13.5	Η,	15.6
Не	24.4	ΗĈΙ	13.8
Hg	10.3	NO	9.5
Na	5.1	N ₂ O	12.9
Ne	21.4	O ₂	12.5
-			
Second Ionization Potentials (eV)			
Ar	27.76	Na	47.0
0	34.93	Cr	16.6
Motostable States			
Species Metestable Species			
пе		19.82	20.01 14 71
Ne Ar		10.02	10.71
Al Vr		0.01	0.00
NI Vo		9.91	9.99
хе		0.31	0.44
Cold Plasma Color			
Argon (violet) Copper (green)			
Oxygen (yellow-white) Sodium (yellow)			ım (yellow)
Nitrogen (red-yellow) Mercury (blue-green)			

and second electron from the atom.

Air (reddish)

If a metastable atom (A*) collides with a different atom (B) which has an ionization energy 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 mixtures. For example,

Ar* (11.55 eV) + Cr^o (ionization energy = 6.7 eV) ==> Ar^o + Cr⁺ + e⁻

Electron collision can also ionize molecular species such as:

$$N_2 + e^- => N_2^+ + 2e$$

The electron-molecule collision can also fragment the molecular

species to form radical (uncharged) species (dissociation) such as:

 $O_2 + e^- => 2 O + e^-$

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

The plasma, therefore, will consist of neutral atoms, excited radiating species, excited metastable species, ionized atoms, electrons, neutral molecular fragments (radicals), ionized molecular fragments, and "new species." In addition, there will be photon radiation (visible and UV) from the plasma. Many of these species will be more chemically reactive than the initial molecular gas species, and the gas species is said to be "activated" in the plasma. 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. 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 highenergy neutrals are unaffected by electric or magnetic fields. The energetic ions and neutrals can lose energy by physical collision with gas species, thereby raising the temperature of the gas.

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. This number density is called the plasma density. The particle temperature of the plasma can vary from a "cold" plasma with a particle temperature of 2–3 eV to a "hot" or fusion plasma with a temperature of several thousand electron volts.

For PVD processing, generally the plasma is cold. At 1 eV particle energy, the electron will have a velocity about 200 times that of an argon ion. In plasma generation, because electrons are accelerated in an electric field, the electron temperature can be significantly higher than the heavy particle temperature in some regions of the plasma.

Sputtering and ion plating are typically performed at about 5 mTorr gas pressure, at which pressure and cold-plasma temperature the particle density is about 10¹³/cm³. A "weakly ionized" plasma might have a plasma density of 10⁸/cm³, whereas a "strongly ionized" plasma might have a plasma density of $10^{12}/\text{cm}^3$, with the balance of the particles being neutrals. The plasma density can be determined by using small-area Langmuir probes, rf attenuation or rf polarization effects. The total energy content (enthalpy) of the plasma is low because of the low plasma density. \Box

Note: The electron volt (eV) is a measure of energy. One electron volt is the energy acquired by a singly charged particle that is accelerated through a potential of one volt. One electron volt is equivalent to a thermal temperature of about 11,000 K (20,000 °F).

Reference

Glow Discharge Processes, Brian Chapmen, John Wiley & Sons, 1980. New York, NY.