New Insights into Aging Phenomena from Plasma Chemistry

Hirotsugu Yasuda

University of Missouri–Columbia, Columbia, MO, USA

Plasma polymerization (deposition of solid materials in plasma) is reviewed with respect to the following aspects:

- Mechanisms of polymer formation in conventional free radical chain-growth polymerization and in plasma polymerization
- Competitive Ablation & Polymerization (CAP) principles
- Plasma sensitivity of elements based on the electro negativity of atoms
- DC discharge polymerization; dark polymerization in the cathode region and glow polymerization in the negative glow
- Effect of electrical field on sputtering & deposition on cathode and anode
- Effect of wall contamination on plasma polymerization.

Summary of Talk: The mechanisms of material formation in plasma polymerization, or plasma chemical vapor deposition (CVD), are completely different from those for conventional polymerizations. Polymeric materials are formed via recombination of free radicals that are formed by fragmentation of molecules caused by the bombardment of energetic species in plasma. Organic compounds can be classified in the following types with respect to polymerization characteristics in plasma: Type 1 monomers are molecules with triple bond and/or aromatic-, hetero-aromatic structures. Type 2 monomers are double bond and/or cyclic structure containing compounds. Type 3 monomers are aliphatic compounds that do not contain structures mentioned in Type 1, and Type 2 monomers. Type 4 monomers are oxygen-containing compounds such as alcohols, ethers, and esters. Plasma polymerization and plasma ablation of materials occur simultaneously in a competitive manner according to the 'Competitive Ablation and Polymerization' (CAP) principle. The balance of these two processes is dependent on conditions of the plasma and on factors of the reactor as well as the types of monomers. DC discharge polymerization consists of dark polymerization in the cathode region and glow polymerization in negative glow. More than 85% of polymerization is due to the dark polymerization, which deposits on the cathode, and polymers formed by the glow polymerization deposits on any surface, including cathode and anode. The anode is a passive surface as far as plasma polymerization is concerned. Characteristics of the cathodic polymer and the glow polymer are significantly different; i.e. cathodic polymers are much tighter networks than the corresponding glow polymers. The deposition mechanisms for glow polymerization and for the dark polymerization are also different. The most important operational parameter for the glow polymerization is W/FM, where W is discharge wattage, F is volume or molar flow rate, and M is the molecular weight of the monomer used, which represents the energy input per mass of monomer gas (J/kg). Most glow discharge polymerizations are carried out in the range of 1 – 1,000 MJ/kg using monomers, which have a total bond energies per mass in the range of 10 – 100 MJ/kg. An overview of plasma polymerization based on the difference of the dark polymerization and the glow polymerization is presented to illustrate the role of electrode surfaces in alternating high frequency discharge (40 kHz and 13.5 MHz). Plasma sensitivity of elements seems to follow the electro negativities of atoms. For example, whether or not F atoms (high electro negativity) of Teflon could be liberated when Teflon is exposed to plasma is determined by the electro negativity of the atom but not by the bond energy of C–F bond. Contrary to the widely spread concept that Teflon is stable even in plasma due to the strong C–F bond, F atoms are liberated from Teflon easily and spread over the entire reactor causing serious problems in certain cases. Since an F atom in a plasma state is reactive, it reacts with surfaces, but the fluorine atoms in the fluorinated surface is labile to plasma and tends to come out of the surface again. Thus, F atoms recycle between solid surface and plasma phase repeatedly. An example of the damaging effect of wall contamination by F-containing fragmented material on the adhesion of nano-film, which is used for corrosion protection of aluminum alloys, is presented to illustrate the importance of the CAP principle and the influence of reactor wall contamination.