

20. Plasma and Silicones

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The use of plasma in conjunction with silicones is a new application field that allows interesting surface modifications.

The term “plasma” covers a broad range of systems whose density and temperature vary by many orders of magnitude. Some plasmas, particularly those at low pressure (e.g., 100 Pa) where collisions are relatively infrequent, have their constituent species at widely different temperatures and are called “nonthermal equilibrium” plasmas. In these nonthermal plasmas the free electrons are very hot with temperatures of many thousands of Kelvin (K), whilst the neutral and ionic species remain cold. Because the free electrons have almost negligible mass, the total system heat content is low and the plasma operates close to room temperature, allowing the processing of temperature-sensitive materials, such as plastics or polymers, without imposing a damaging thermal burden onto the sample. However, the hot electrons create, through high energy collisions, a rich source of radicals and excited species with a high chemical potential energy capable of profound chemical and physical reactivity. It is this combination of low temperature operation plus high reactivity that makes nonthermal plasma technologically important and a very powerful tool for manufacturing and material processing.

These properties provide a strong motivation for industry to adopt plasma-based processing, and this move has been led since the 1960s by the microelectronics community, which has developed “low pressure glow discharge plasma” into a high technology engineering tool for semiconductor, metal and dielectric processing. The use of plasma to deposit thin dielectric films is often referred to as plasma-enhanced chemical vapour deposition (PECVD) processing.

Various precursors are available, specifically designed for the deposition of thin film dielectrics via PECVD and compatible with copper dual damascene and aluminum interconnect processes. These precursors are:

- Gases like Me_3SiH , which can be used with processing technology developed for silane-based dielectric film deposition
- Liquids like Me_4Si , $(\text{SiHMeO})_4$ and $\text{SiMe}_2(\text{OMe})_2$, which can be used with processing technologies developed for TEOS-based dielectric film deposition

Typical thin-film dielectrics formed by these precursors include silicon-carbide (a-SiC:H), silicon-oxycarbide (a-SiOC:H) and silicon-nitride (a-SiCN:H). Typical applications include interlevel dielectric, copper diffusion barrier, etch stop, hard mask, low-k interlevel dielectric, gap fill, and passivation.

Vacuum or low-pressure plasma has increasingly penetrated other industrial sectors since the 1980s, offering processes such as polymer surface activation for increased adhesion/bond strength, high quality degreasing/cleaning and the deposition of high performance coatings. However, due to operation at reduced pressure, processing is restricted to batch wise or at best is pseudo-continuous and thus not applicable to in-line production. Therefore, newly developed atmospheric pressure plasmas offer industry open port or perimeter systems

providing free ingress into and exit from the plasma region by work-pieces/webs. Hence, atmospheric pressure plasma offers new continuous, on-line processing capability for many industrial sectors, such as textiles, packaging, paper, medical, automotive and aerospace.

The work of Okazaki et al. in the 1980s showed that a stable glow discharge could be readily formed at atmospheric pressure [1-2], which ignited a volume of research and a wide variety of plasma systems that now operate at atmospheric pressure. The early work by Okazaki focused on generating plasmas using helium as the process gas. Later this was extended to include argon and nitrogen. Further developments have produced atmospheric pressure plasmas in a wide variety of gases, including air [3]. The exact conditions employed vary depending upon the gas, electrode geometry and other factors. Typically these ambient temperature atmospheric pressure plasmas are referred to as diffuse dielectric barrier discharge [4], a term generally used to cover both glow discharges and dielectric barrier discharges that are homogeneous plasmas across the width and length of a plasma chamber [5].

Technology is now available to combine unique precursors and their delivery into an atmospheric pressure plasma operating at ambient temperature to achieve deposition. This process is known as atmospheric pressure plasma liquid deposition (APPLD). Such APPLD equipment comes in two configurations:

- Large-area plasma for processing flexible webs such as textiles, nonwovens, paper, films and foils, fibres, thread, yarn or filament
- Jet plasma for processing three-dimensional, rigid sheet materials or material in fibre/filament form

By directly injecting an aerosol of liquid precursor into a homogeneous atmospheric pressure plasma, a thin conformal layer of polymerised coating can be deposited onto a substrate surface that is in contact with the plasma. Typically, these coatings are some tens of nanometres thick. The combination of liquid precursor and diffuse atmospheric pressure plasma ensures that this process retains all the original functional properties of the liquid precursor – even for large, complex molecules. This is a property unique to APPLD, as almost all other atmospheric pressure plasma processes destroy complex precursors (see Figure 1).

This enables tailoring of the surface chemistry with a specific chemical functionality and/or a specific surface response. This surface engineering can be applied to a variety of different substrate classes for a wide range of applications. Thus, advanced surface properties that include biofunctionality, oil repellency and adhesion promotion are now available from APPLD technology, offering the prospect of plasma processing penetrating a wide range of new, high-value industrial applications.

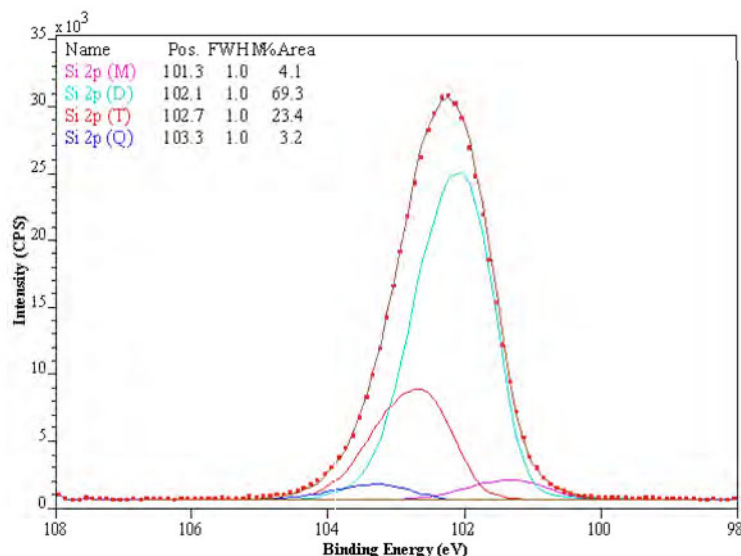


Figure 1. XPS (ESCA) spectra of a polyester film after plasma treatment with a polyhydrogenmethyl siloxane polymer precursor, $M(D^H)_nM$, using the APPLD technology. The presence of peaks corresponding to T and Q units indicate that some modification of the original polymer has occurred, leading to cross-linking. But most of the polymer's original functionality remains as indicated by the strong peak corresponding to D^H units.

Due to the unique nature of the APPLD process, a wide variety of silicones can be utilised as precursors to provide specific surface properties. For example, polydimethylsiloxane (PDMS) polymer coatings are widely used [6] for their excellent hydrophobic properties, which increase water repellency, release and “handle.” Tetramethylcyclotetrasiloxane and octamethylcyclotetrasiloxane have been successfully used as precursors to produce polysiloxane coatings, which have been shown to provide a water contact angle of 140° on a cotton substrate, whereas a water droplet applied to nontreated cotton wets out immediately (see Figure 2).

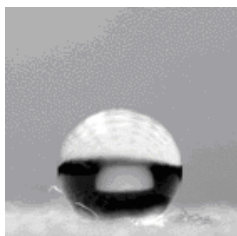


Figure 2. A water droplet on a silicone plasma treated cotton fabric. (Picture courtesy of Dow Corning Plasma Solutions.)

In oxidising plasma conditions, low molecular weight PDMS precursors are converted to silica-like (SiO_x) coatings. The APPLD process is an alternative route to depositing organosilane molecules, without the requirement of using water or organic solvents.

References

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This article has been published in the chapter "Silicones in Industrial Applications" in *Inorganic Polymers*, an advanced research book by Nova Science Publishers (www.novapublishers.com); edited by Roger De Jaeger (Lab. de Spechtrochimie Infrarouge et Raman, Univ. des Sciences and Tecn. de Lille, France) and Mario Gleria (Inst. di Scienze e Tecn. Molecolari, Univ. di Padoa, Italy). Reproduced here with the permission of the publisher.