

1. Introduction

It has been known since the beginning of the 1960's that surfaces exposed to an electrical discharge, operated in a gaseous atmosphere containing organic vapors or gases, are covered with insulating deposits. These deposits were in the form of pinhole-free thin films, were chemically and thermally stable, and were insoluble in organic solvents [1, 2]. These deposits, now known as plasma polymers or plasma deposits, were immediately brought into application when plasma polymerized styrene was used as dielectric separating film. During the next thirty years plasma polymerization was recognized as an established and rapidly developing field with basics laid down in publications by the groups of M. Shen, A. T. Bell, H. Yasuda, R. d'Agostino and others [e.g. 3-5].

Starting from the 1970's investigators initiated discussions of the effects of discharge conditions such as polymerization time, monomer pressure, discharge current, discharge power, and substrate temperature on the plasma polymerization rate. Since then the structure of plasma polymers has been examined by a number of different methods. Several investigators postulated networked structure of plasma polymers, e.g. of plasma polymerized ethylene as proposed by Tibbitt [6]. Eventually it became clear that a network of a plasma polymer has no repeating unit but it contains a number of various groups. The structure is branched and randomly terminated with frequent cross-links. To obtain a better control over the structure of the plasma polymers pulsed plasma polymerization was introduced during the 70's by Tiller [7]. The advantages of using r.f. pulsed plasma over continuous wave plasma has since been discussed in various studies [8-10]. Yasuda and Hsu [11, 12] used electron spin resonance spectroscopy and XPS to determine the effects of pulsed RF discharges on polymer deposition. They studied plasma polymerization by comparing the use of hydrocarbons and perfluorocarbons. In 1979, Nakajima et al. [13] studied the plasma polymerization of tetrafluoroethylene. Here they found that it was possible to control the functional groups formed on the surface of the deposited polymers by varying the deposition conditions. It was also found that the networked structure of the plasma polymers contain a large concentration of trapped free radicals. At this time studies were also aimed at the reduction of radical concentration in the polymers by the use of low powers and pulsed plasmas [11]. These radicals had been shown to react with atmospheric oxygen to form oxygenated species such as carbonyl and hydroxyl groups [14].

Eventually interests were raised in the field of specifically 'tailored' films with technologically relevant properties. The functional groups that were of most interest to the scientists were the hydroxyl, carboxyl and amine groups. Allyl alcohol is one of the most extensively studied monomer starting from the late 1980's. Ameen et al. [15] studied the effect of monomer flow rates on the chemical character of the prepared plasma polymers and concluded that using the higher monomer flow rates results in a high retention of hydroxyl groups. O'Toole et al. [16, 17] investigated the effect of power on functional group retention for several plasma polymers and suggested that the competition between the processes of oligomerization and fragmentation can be mediated by a choice of electrical power, giving a degree of control over the chemistry of the product. These observations were supported by other investigators [e.g. 18, 19]. Friedrich et al. [18] also attempted the variation in the density of functional groups on the surface of plasma polymers via copolymerization of functional group carrying monomers with either a chain extending monomer such as ethylene or a cross linker such as butadiene.

Scores of papers have been published during past two decades on the study of plasma polymerization of various other compounds. Most of them have been focussed on the effect of variation in the Yasuda factor [2], power and duty cycle. The compounds studied include styrene, the series of methacrylate monomers, a series of vinyl sulphones etc. In general low values of Yasuda factor and power have shown a greater retention of structures from the monomer in the plasma polymers. Similar observations of a high retention of the monomer structure at low values of Yasuda parameter were reported by Inagaki et al. [20] when they used a mixture of carbon dioxide with acrylic acid for depositing plasma polymers.

A majority of studies reported here used a multi-method approach owing to the complexity in characterization of the plasma polymers. XPS was one of the most widely used methods in combination with FTIR, ToF-SIMS and mass spectroscopy. XPS along with NEXAFS was also used by Retzko et al. [21]. The authors focussed their investigation on the comparison of plasma deposited polymers with conventional polymers and the variation in deposition rates between plasma deposited films of different monomers.

In spite of a lot of work been done in the field of plasma polymerization during last decades, often serious drawbacks like chemical changes on exposure to air or nonuniformity (chemical or physical) and a limited understanding of the polymerization process itself prevents a broader application. Hence it is worth putting efforts into investigations for improvements of plasma polymerization processes. Answers are required

especially on how deposition parameters influence the resulting properties of the plasma polymers.

Additionally, most of the studies in the past were based on the characterization of plasma polymers only after they were prepared and then exposed to air before transferring them into vacuum for analysis. Due to the presence of a large amount of trapped free radicals, post-plasma reactions change the surface properties of the plasma polymer to a large extent. It therefore becomes difficult to get a real picture of the “as deposited” chemical structure of the plasma polymers. Hence it is important to study the deposited polymers also before exposure to air.

The aims of this work are the following:

- a) To improve the understanding of the plasma polymerization process,
- b) To investigate the effects of various external plasma parameters on the chemical character of the plasma homopolymers and copolymers,
- c) To investigate the aging process of different plasma polymers, and
- d) To demonstrate the efficient use of XPS and NEXAFS as complimentary tools in the surface analysis of plasma polymers.