1. Introduction

Non-equilibrium plasmas of volatile organic compounds may be used to deposit ultra-thin, pinhole-free films. These films are commonly referred to as plasma polymers or plasma deposits. The approach is attractive as it affords control over film chemistry and thickness, and film deposition is uniform and takes place within a clean environment, i.e., without any use of solvents. Plasma process provides an important and powerful technique for altering the surface chemistry of materials without changing their bulk properties. Therefore they have been used for a wide variety of applications ranging from electrical devices to medical implants.

In many cases, polymers formed by plasma polymerization are different in chemical composition, and structure as well as physical properties e.g., conductivity, from those formed by classic polymerization, even if the same monomer is used. The structure of plasma polymers are rather complex. They are to some extent unsaturated, branched and cross-linked. In a plasma polymerization process the chemical structure of the plasma polymer can be altered by a selection of external plasma parameters, e.g., duty cycle and plasma power. The characterization of plasma polymers and the investigation of their structural dependence on the external plasma parameters require a multi-method approach. The correlation of relevant external plasma parameters with the primary chemical structure of the plasma polymers is the subject of a dedicated research project launched in the BAM laboratory VIII.23, “Surface and Thin Film Analysis”. This project is focused on correlations between the chemical character of the plasma deposited polymer films and the variation of external plasma parameters. These are pulsed or continuous wave (CW) plasma condition, duty cycle in pulsed plasma, plasma power, monomer flow rate, reaction pressure, and the ratio of monomer partial flow rates in co-polymerization. Co-polymerized products are of special interest because it is assumed that technologically requested film properties may be “tailored”. Monomers to be used are simple organic molecules with a polymerizeable C=C bond, styrene, ethylene, allylamine, and allyl alcohol. Chemical properties of interest are the unsaturated, branched and cross-linked character of the films, as well as the retention of the respective monomer functionality. This study is concerned with the investigation of the basic chemical character of the plasma polymers by means of time of flight - static secondary ion mass spectrometry (ToF-SSIMS). SSIMS is a surface sensitive method and there is a direct relationship between surface structure and the fragmentation pattern observed in SIMS. It will be shown that

SIMS may provide information on the unsaturation, branching and cross-linking, as well as aromatic and aliphatic content of plasma deposited films. SIMS is probably the only *surface* analytical method which may provide information on branching and cross-linking. XPS (X-Ray Photoelectron Spectroscopy), a complimentary method of surface analysis and most often used for surface characterization of polymers, can not provide this kind of information.

A special issue of this study was to characterize freshly deposited films immediately without any exposure to ambient air. A specially designed experiment enables that "in-situ" analysis. The effect of exposure to air itself, i.e., the post-plasma ageing process, was also investigated in detail by another dedicated experiment. Here, the samples were exposed to air in a well defined scheme. The oxygen uptake, the formation of oxygen species due to ageing and the effect of external plasma parameters on the oxygen uptake related changes of the plasma polymers are the topics of interest.

This thesis will start with some theoretical background information. Experimental methods are outlined in Chapter 3. Information on the SIMS methodology and ToF-SIMS instrument is given in Chapter 4. The results obtained through in-situ characterization of plasma polymers and copolymers are presented and discussed in Chapter 5 and Chapter 6, respectively. The ageing behaviour of plasma polymers and copolymers are presented and discussed in Chapter 7. Finally, general conclusions are drawn in Chapter 8.