I. INTRODUCTION

Glow Discharge induced Sublimation (GDS) is a method for the growth of thin polyimide films, which has been recently added to the more widely used spin coating, dip coating, vacuum evaporation and ionized cluster beam deposition. GDS has been successfully used for the deposition of PMDA-ODA polyimide films [1]. More recently the GDS deposition of several precursor monomers to be used in the synthesis of polyimides to be applied in radiation detectors [2] has been investigated.

In this work the damage of the monomer molecules induced by ion bombardment and the subsequent incorporation of molecular fragments in the deposited films are studied by x-ray photoelectron spectroscopy (XPS). The monomers selected for this work were those studied in [2], i.e. 2,4,6-trimethyl m-phenylenediamine (TMPD), 3,3'-diaminodiphenyl sulfone (DDS), 4,4’-hexafluoroisopropylidene dianiline (6FDAm), 3,3’,4,4’-biphenyltetracarboxylic acid dianhydride (BPDA) and 4,4’-hexafluoroisopropylidene diphthalic anhydride (6FDA). Since XPS is a powerful tool for the characterization of the chemical composition of the first nanometers of material surfaces, it has been used to get information on the molecular species deposited precisely at the end of the deposition. Monomer powders were also used as reference samples for XPS analysis.

II. EXPERIMENTAL

The experimental equipment used for the coatings deposition has been described in [3].

XPS analyses were performed using a Kratos AXIS-HS spectrometer equipped with Mg kα1,2 (1253.6 eV) x-ray source (10 mA, 15 keV). The instrumental transmission operates in fixed analyser transmission (FAT) mode. A pass energy of 40 eV was selected which allows an intrinsic full width at half maximum (FWHM) of 0.8 eV. To deconvolute the various peak components, a Gaussian curve fitting procedure was made after linear background subtraction. Quantitative data were obtained from the experimental peak area using a computer routine based on empirically derived atomic sensitivity factors.

III. RESULTS

A comparison between the C1s peaks of the TMPD samples (powder and film) shows the decrease of the component at 286.5-287 eV, which is assigned to C-NH2, and the decrease of the “shake up” satellites due to the π* ← π transition in the aromatic moiety in the TMPD film. In particular the atomic ratio between C-C (285 eV) and C-NH2 increases from 3.6 (powder) to 8.2 (film) and the ratio between C-C and N from 3.5 to 6.6. Moreover the atomic ratio C/N increases from 4.5 to 7.7. All these data point out the loss of an amine group from the TMPD molecule.

XPS analysis also points out the presence of oxygen in the TMPD film (6 at. %), which is thought to be either adsorbed water or oxygen coming from the amine oxidation.

FIG. 1: S2p spectra of DDS powder (upper) and film (lower).

XPS analysis of DDS film confirms the very pronounced damage, which mainly pertains to the central part of the molecule as shown by the S2p spectrum (Fig. 1): the S peak in the SO2 group (168-168.5 eV ) is very small while a new peak appears at about 164 eV, due to elemental S or to organic sulphides (R-S-R'). A partial S loss occurs as shown by the increase of the C/S atomic ratio from 12 (powder) to 14 (film). The analysis of the C1s peak shows that the component centred at 286.6 eV, which is assigned to Ar-SO2 and Ar-NH2, is more pronounced in the film than in the powder; moreover a new component appears at 288 eV and is assigned to the...
C=O group or to other carbon containing groups with similar chemical shift coming from the precursor oxidation. Taking into account the loss of SO2 groups, the high intensity of the component at 286.6 eV can be explained by assuming the presence of C-O bonds, which is also suggested by the increase of the O percentage (in spite of the S decrease) and by the appearance of the peak at 288 eV. The C-O bond can arise from the oxidation of aniline radicals produced by the C-SO2 bond breaking. The increase of C/N atomic ratio from 6 to 7.7 suggests another reaction path for the formation of C-O bond: the NH2 group is lost during the deposition and then partially replaced by O after air exposure.

Similarly to DDS, the damage mainly interests the central part of the 6FDAm molecule and it involves the loss of CF3 groups: in fact the atomic ratio between C of CF3 group and C not bonded to bridging C decreases from 0.2 (powder) to 0.06 (film); the component at about 291.3 eV (due to bridging C superimposed on the shake up band) becomes comparable to the background noise and the C/F atomic ratio increases from 2.5 to 5.2. The loss of NH2 groups also occurs as shown by the increase of C/N ratio from 7.5 to 10.4.

A high O content (16 at. %) is also detected: besides the appearance of the O1s peak, the C1s peak can be fitted by assuming the presence of other two new components at about 288 eV and 289 eV, which are assigned to >C=O and (C=O)-O- bonds arising from air exposure of the deposited film. Moreover the component at 286.5-286.6 eV, assigned to the phenyl C bonded to the bridging C and to Ar-NH2 in the powder, is thought to be mainly due to C-O, which has comparable binding energy. As a matter of fact, the loss of CF3 groups and the breaking of the bond between bridging C and phenyl rings should cause a decrease of this peak, but this does not occur suggesting the presence of C-O bonds arising either from the oxidation of aniline radicals or from replacement of NH2 similarly to DDS.

For BPDA the damage is concentrated in the anhydride rings: CO/(CO)-O groups have been lost during the deposition, as shown by the decrease of the atomic ratio between carbonyl C (289 eV) and phenyl C (285 eV), which goes from 0.33 down to 0.07 in the deposited film (Fig. 2). After air exposure the film surface contains COOH groups and other groups such as R-CO-R', C-O-C as a result of the monomer damage, as shown by the appearance of two new components at 288.4 eV and 287.8 eV in the C1s spectrum. The presence of C-O bonds can be due to the oxidation of (CO)x-lacking BPDA molecule. The strong decrease of the shake up bands in the spectrum of the BPDA film is an additional confirmation of the monomer damage.

O1s spectra show that the atomic ratio between oxygen in the carbonyl (532.2 eV) and bridging-bonded (533.4 eV) decreases from 2 to 1.7 in the film. This result is in agreement with a partial decomposition of anhydride groups in the BPDA molecule.

Similarly to BPDA the damage of 6FDA molecule is concentrated on the anhydride rings, with the loss of CO/CO2 groups. The C1s spectrum of 6FDA powder can be fitted using five components centred at 285 eV (assigned to carbon of phenyl rings), 286.6 eV (assigned to phenyl C bonded to bridging C), 289 eV (carbonyl C in the anhydride groups), 290.5-290.7 eV (assigned to bridging C) and 292.5 eV (C-F). In the 6FDA film the atomic ratio between carbonyl C and phenyl C not bonded to bridging C decreases from 0.5 to 0.1. On the contrary, the decrease of the peaks of bridging C and C-F is much lower, indicating a minor damage of the central part of the molecule. This is confirmed by the F1s spectrum: the peak at 688 eV (F-C) is only slightly decreased, giving rise to ionic fluorine (686 eV).

**FIG. 2: C1s spectra of BPDA powder (upper) and film (lower).***

In the C1s spectrum of 6FDA film two new components are also visible: the former at 287.6 eV is due to groups absent in the pristine monomer molecule (e.g. Ar-(C*=O)-Ar' or para-benzoquinone-like structures); the latter component at about 284 eV is assigned to amorphous C. The appearance of these components confirms the presence of more damaged structures in the 6FDA film. Similarly to BPDA a slight increase in the relative intensity of the O1s component centred at 533.4 eV with respect to the component centred at 532.2 eV is observed as a consequence of a partial decomposition of anhydride groups.