PLASMA POLYMERIZATION OF 2-IODOTHIOPHENE

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Abstract

Plasma polymers deposited from 2-iodothiophene in a microwave plasma reactor are analyzed by XPS and FTIR. To get direkt information about the fragmentation mechanism in the plasma optical emission spectroscopy (OES) was used. The electrical conductivity of the coatings was measured.

The plasma polymer coatings had an electrical conductivity up to 10^{-1} Scm^{-1}. Concerning the oxidation stage of the iodine, I_3^- and I_5^- were identified as the dominant spezies by XPS. The FTIR-spectra of the deposited plasma polymers showed a good similarity to that of electrochemical, deposited poly(thiophene). This is a strong indication that their chemical structur is similar to that of electrochemical deposited films.

Introduction

Plasma-chemical processes are applicable in various technical fields, such as electronics, biochemistry, materials science, etc.. The processes are deposition, surface modification, and etching. The application of surface modification and etching will be discussed in two other papers of our research group /1,2/, therefore this paper will deal with an application of plasma polymerized coatings.

The properties physical (elctrical conductivity, adhesion, dielectric) and chemical (hydrophilic and hydrophobic) of conventional polymers are strongly dependent on the nature of the starting monomer. In contrast to that, the structure of plasma polymerized coatings depend not only on the monomer stucture. The most significant difference is that the plasma polymers are crosslinked. Plasma polymerized coatings are usually not electrically conductive, even if the conventional polymers prepared from the corresponding monomers are electrically conductive. But it has been possible to deposite intrinsically conductive coatings by plasma polymerization.

Usually the conductivity of these intrinsically conducting coatings is quite low (10^{-12} - 10^{-17} S cm^{-1}) /3/. It can be improved by oxidation, e.g. with iodine or reduction, e.g. with sodium.

We have started to develope a plasma-chemical process to prepare intrinsically conductive coatings. The oxidant iodine was introduced into the plasma together with the monomer, using a monomer, which contains covalent bounded iodine. Therefore the relation between the iodine and the monomer is constant over the whole set of parameters. 2-Iodothiophene, a monomer which contains weakly bounded iodine has been choosen as a model monomer for our plasma process.

The chemical structure of the films was investigated by XPS and FTIR; the electrical conductivity was measured by the two probe technique. The plasma process itself was examined with the optical emission spectroscopy to get in-situ-information about the fragmentation mechanisms.

Experimental

The coatings are prepared in a microwave vacuum system (Fig.1). After the argon flow rate (6 - 12 sccm/min) is adjusted the monomer, placed in a heated reservoir, is introduced by opening a needle valve and polymerized by a MW discharge of 2.45 GHz. The total pressure in the plasma chamber during polymerization is 0.32 ± 0.02 mbar andcontinuously monitored. If necessary the pressure is automatically adjusted by throtling the pumping pipe.

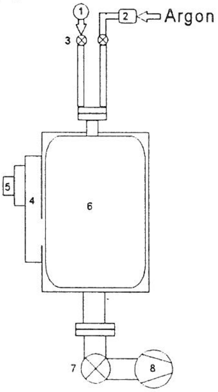

Fig.1: Schematic view of the plasma reactor: **1** monomer **2** mass flow controller **3** needle valve **4** wave guide **5** magnetron (microwave 2.46 GHz) **6** plasma reactor (10 dm^3) **7** butterfly valve **8** pumping pipe

The plasma power was varied between 210 and 300 W to study the effect of power on the polymerization process. Substrates (silicon for XPS, NaCl plates for FTIR and glass plates for conduction measurements) are placed in the center of the reactor.

The optical emission spectra were recorded with an EG&G PARC OMA modell 1235 detection system. A Spectra Pro 275 spectrograph (Czerny-Turner type) with a focal length of 0.275 m from Acton Research Corporation was connected. The resolution of this system can be tuned to 0.075 nm, using 1200 g/mm grating and a 25 μm slit.

X-ray photoelectron spectra are recorded on a VG Escalab MKII spectrometer (triple channeltron) using a MgKα radiation (12 kV, 10 mA, CAE mode). The base pressure in the spectrometer was $2*10^{-10}$ mbar. Core level spectra are calibrated with reference to the Cls core level peak located at 285.0 eV.

A Nicolet FTS 740 spectrometer is used to record transmission spectra of the plasma polymerized coatings as directly deposited on NaCl plates.

Results and Discussion

Optical emission spectroscopy (OES)

Light emission of the plasma was monitored through a view port (Spectrosil B®) of the plasma reactor. An almost homogeneous distribution of the emission was detected with exception of a small region of 1 cm near the wall of the vessel, where a smaller emission intensity was observed.

Due to the fact that optical emission is the result of a complex plasma chemical process, including e.g. ionized and excited species. It is well known that a comprehensive characterization of a deposition process very difficult. A big number of species, which can be essentially involved in the film growth process are undetectable by this method because they do not emit photons.

Nevertheless, OES has been proven to be a valuable tool for plasma characterization, giving significant information e.g. about fragmentation mechanisms of the monomers.

Fig. 2 depicts a typical emission spectrum (spectral range 450 - 890 nm). The most prominent emission lines are attributed to the carrier gas argon. In the enlarged part (450 - 690 nm) of the spectrum most other emission lines corresponding to iodine /4/, indicating that one of the fragmentation mechanisms is the split off of iodine from the aromatic ring. The remaining emission lines belong to atomic hydrogen, which is always observed when organic monomers are involved in plasma processes. Spectral lines of sulphur, which is contained in the aromatic ring structure were not observed.

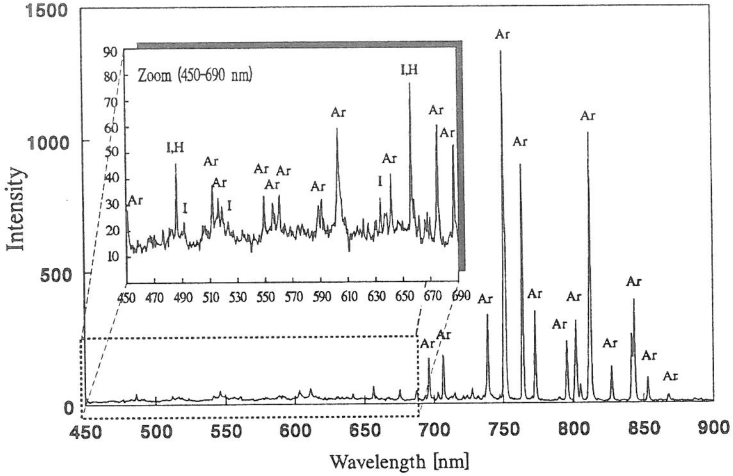

Fig.2: OES spectrum of a 2-iodothiophene/argon microwave plasma

X-ray photoelectron spectroscopy

XPS analysis was performed of films deposited in the reactor at different powers (210 - 300 W), different pressures (0.25 to 0.45 mbar) and different argon flow rates (3 - 12 sccm). The atomic composition of the deposited plasma polymerized coatings compared to the composition of monomer is very important for the assessment of the coatings. In fig. 3 a survey-spectrum of plasma polymerized 2-iodothiophene is given and the corresponding elemental composition is listed in Tab. 1. Content of hydrogen (33.3 at% in the monomer) was not taken into account, due to the disadvantage of the XPS method to detect it. Also a small amount of oxygen (less than 3 % at the surface) is not listed in this table, because it does not belong to the coating process itself. The angular dependency of the O1s-emission (0° and 70°) shows that the oxygen is enriched on the surface.

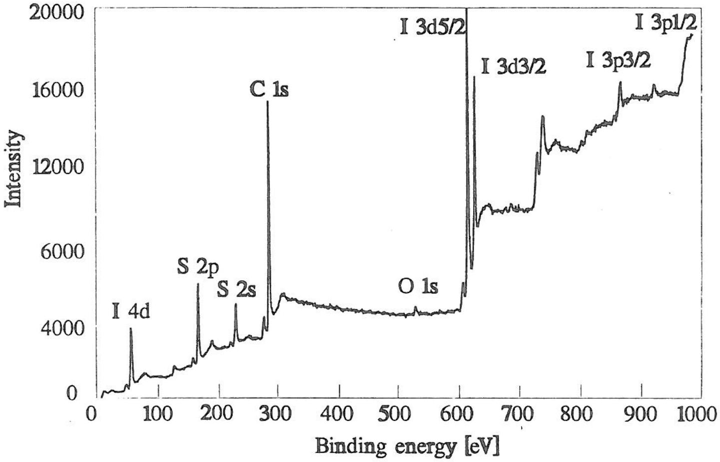

Fig.3: XPS-Survey spectrum of plasma polymerized 2-iodothiophene (MgKα 1253.6 eV, 12 kV, 10 mA, normal emission, pass energy 50 eV)

Tab.1: Results of the XPS analysis: Atomic composition of the monomer and a plasma polymerized coating (300 W, 0.35 mbar)

	Composition [at%]	
Species	Monomer	Plasma polymer
Carbon	66.6	76.4
Sulphur	16.7	14.8
Iodine	16.7	5.8

The content and the chemical state of iodine is of special interest for the electrical properties. In contrast with earlier experiments /5/ the decrease of the sulphur and iodine content, compared with the monomer, is low. Compared with earlier experimental set-up the linger time of the gases in the plasma reactor is changed, which could be the reason for the different results.

The various components of the $I3d_{5/2}$ core level are shown in fig. 4. An explanation of the origin of these peak is not easy to find because of the small chemical shifts. Besides the monoiodine ion I^- several forms of anions are known. Among these I_3^- and I_5^- are the most important ones /6/. In the literature /7-12/ various states of iodine in conventional and also in plasma polymers are discussed and their binding energies have assigned to each state. For the identified species I_3^- and I_5^- and covalently bound iodine, binding energies of 619.0±0.3 eV, 620.5±0.3 eV and 621.0±0.3 eV were determined.

With this information a peak synthesis of the I3d5/2 emission peak was performed using the standard VG software. The result of the peak fit, that the dominating species are the I_5^- ion and covalently bound iodine.

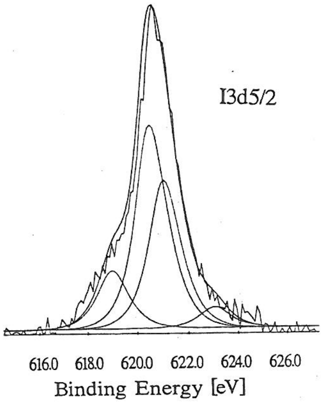

Fig. 4: XPS detail spectrum of I $3d_{5/2}$ (MgKα 1253.6 eV, 12 kV, 10 mA, normal emission, pass energy 10 eV)

Infrared spectroscopy

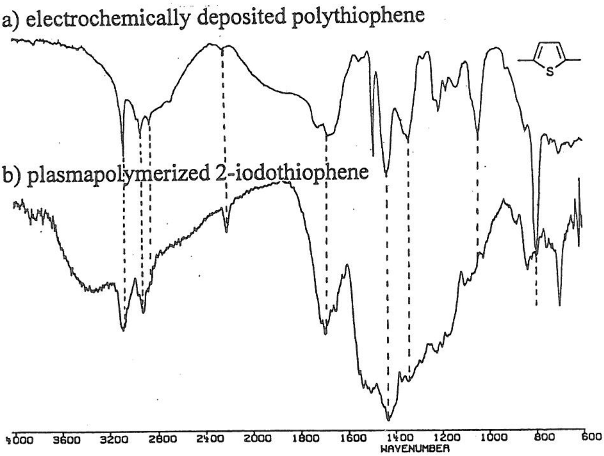

Fig.5: IR spectra of a)electrochemical deposited poly(thiophene) and b)plasma deposited 2-iodothiophene

Infrared spectra of poly(thiophene) and plasma polymerized 2-iodothiophene are presented in fig. 5. Compared to the infrared spectrum of the electrochemically deposited poly(thiophene), the bands in the spectrum of the plasma polymerized polymer are broadened and some new bands appear. These characteristic phenomena can be explained by the typical molecular structure of plasma polymers. The spectra features the 2-iodothiophene plasma polymers can be assigned to the following molecular groups and monomer components. At 3100 cm^{-1} the C-H stretching vibration of the hydrogen bound in aromatic thiophene ring is present, indicating that a marked amount of this chemically stable structure is conserved in the deposited film. The stretching vibration of methyl- and methylene groups can be found at 2900 cm^{-1}. The noticeable structure at 2200 cm^{-1} is possibly be assigned to a C≡C-bond of a fragment from the thiophene ring, which may be build by a hydrogen elimination reaction, comparable to equivalent spectral features in poly(ethylen(3-butyl-2,5-thiophenediyl)ethynylene) /13/. The C=O stretching, formed by the reaction of unsaturated radicals on the surface of the coatings with oxygen and water and the C=C stretching leads to an absorption of a stretching mode at 1700 cm^{-1}. Of special interest with respect to the oxidant is the infrared-band near 860 cm^{-1}, which is connected to the C-I bonding.

A characteristic absorption for thiophene can be seen near 700 cm^{-1}. In comparison to the unoxidized poly(thiophene) this structure is shifted to lower wavenumbers, due to the electronegative iodine. In general, reasonable similarity can be clearly seen between the spectra of plasma polymerized 2-iodothiophene and that of electrochemical deposited poly(thiophene).

It could be shown that it is possible to maintain the configurational feature of the monomer unit (thiophene ring) in the plasma polymer, if the polymerization is performed at low specific energies.

Conclusion

XPS and IR analysis show that the plasma polymerization of 2-iodothiophene and argon occurs by a mechanism, involving e.g. ring opening and cross linking reactions. By this process homogeneous plasma polymerized coatings (50 - 400 nm) were obtained, showing good electrical conductivity of up to 10^{-1} S cm^{-1}. The presence of some infrared absorbtions associated with normal modes of vibration of the thiophene ring show that the fragmentation of the aromatic ring is not the major process leading to the formation of the polymer.

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