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ISOLATED PLASMA ION BEAM DEPOSITION OF POLYMERIC FILMS AND IN-SITU CHARACTERIZATION BY ELECTRON SPECTROSCOPY

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Polymeric films have been prepared from different monomers (styrene, benzene, HMDSO) in a preparation chamber of an electron spectrometer under UHV conditions by means of a special plasma polymerization technique (IPIBD). This method allows an independent control of the plasma parameters and of the energy of the deposited ionized molecule fragments. As deposited films have been characterized by electron spectroscopy measurements (UPS, XPS, EELS) and are compared with condensed monomer films. Polymeric films prepared by standard rf plasma polymerization (RFPP) have been deposited as well. IPIBD- and RFPP-films have been characterized in addition by pyrolysis/mass spectrometry and IR spectroscopy.

Isolated plasma ion beam deposition (IPIBD) has been applied to deposit polymeric films on Au, Si and Ge. Several monomers (styrene, benzene, HMDSO) has been used as process vapour. The preparation was performed in an UHV preparation chamber connected to an electron spectrometer (Leybold, EA 10/100 and 11/100). A plasma is generated within a single grid broad beam ion source by means of energetic electrons and a discharge voltage U_A applied between the tungsten filament and the anode. The as produced ionized molecule fragments are accelerated by an electric field applied between the plasma chamber and the accelerator grid. The main advantage compared to conventional r.f. plasma polymerization (RFPP) is the precise control of the kinetic energy E_I of the impinging ion fragments which has been varied from 20eV to 900eV. In addition this method allows the local separation of the plasma and the substrate and the independent control of the plasma generation and ion deposition.

The films have been characterized by electron spectroscopy measurements. In particular UPS turned out to be a very sensitive tool to investigate tiny changes between films deposited with different parameters. Differences in the UPS valence band (VB) spectra are closely related to changes in the atomic structure of the films.

For comparison condensed films have been studied on a cold Au substrate (T=80K).

The results obtained from polymeric styrene films are discussed here as a typical example. Figure 1 shows the UPS VB spectra of the condensed solid styrene film and a sequence of polymer films with different deposition parameters. The VB of the condensed film consists of several peaks (A_1 to D_2) which can be interpreted in terms of molecular orbitals as discussed in [1]. Comparing the polymeric film (E_I=20eV, U_A=50V) with the condensed film, peaks A_1 and A_2 split due to the attachment of the ethylenic group in the styrene molecule, degenerate to peak A in the IPIBD films which can be attributed to the polymerization process involving the removal of the ethylenic double bond. This can also be observed in the disappearance

of the ethylenic π peak B in the IPIBD films. Further, the development of the IPIBD film VB spectum as a function of the kinetic energy of the ion fragments was studied. With higher kinetic energy the phenylic peak A has strongly decreased in intensity, indicating a breaking up of benzene rings in the deposited films. This trend could also be confirmed by IR measurements (Fig.2) by determining the ratio of aromatic to aliphatic C-H vibrations. The IPIBD films were also characterized by pyrolysis/mass spectrometry in order to study the degree of polymerization. Figure 3 shows a corresponding spectrum of an IPIBD film with E_I=270eV. Keeping in mind that the atomic mass of styrene is 104, masses up to 368 have been found indicating a considerable cross linking of the IPIBD films.

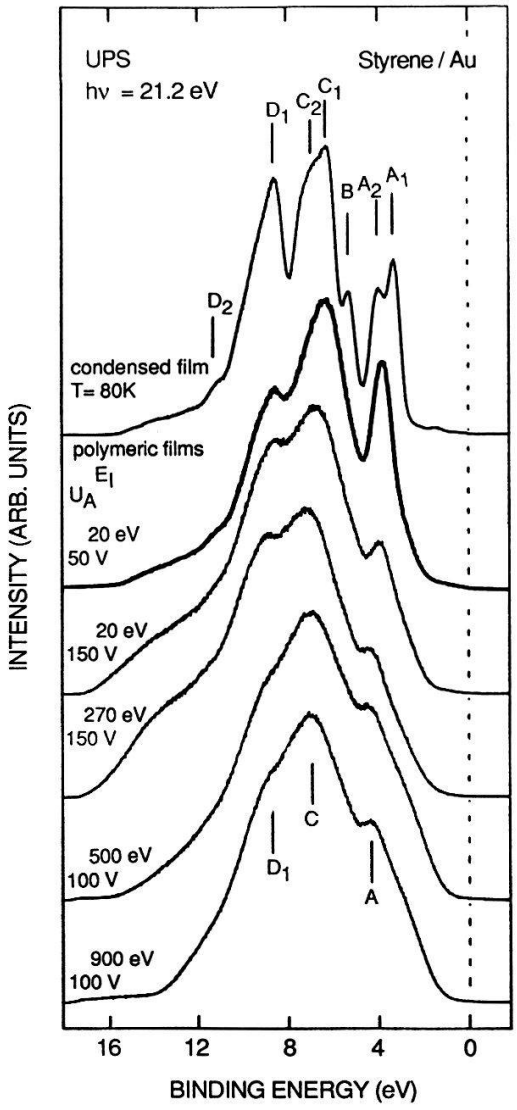

Fig. 1: UPS VB spectra of a condensed styrene film and a sequence of polymeric IPIBD films.

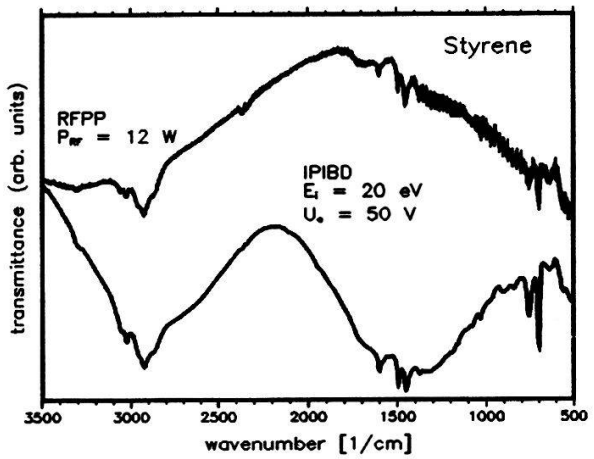

Fig. 2: IR spectra of an IPIBD film (E_I=20eV, U_A=50V) and RFPP film (P_{rf}=12W).

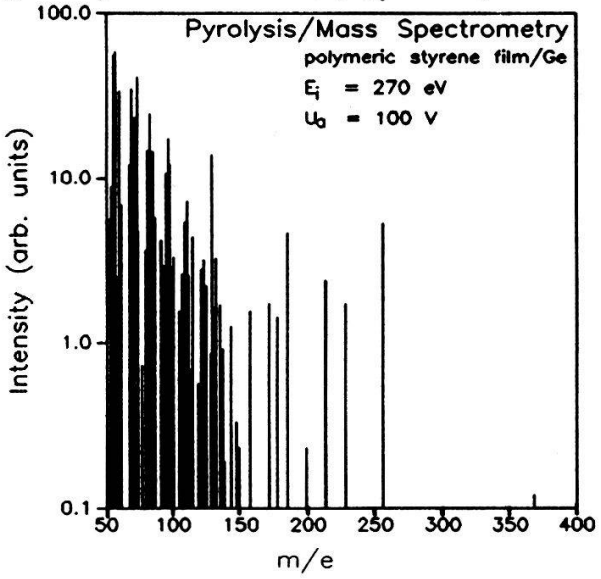

Fig. 3: Pyrolysis/mass spectrometry of an IPIBD film (E_I=270eV, U_A=100V).

In conclusion, we have shown that polymeric films can be prepared by the IPIBD technique and that the electronic and atomic properties strongly depend on the kinetic energy of the impinging ion fragments.

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[1] J.W. Rabalais and R.J.Colton, J. Electron Spectrosc., 1, 83 (1972/1973)