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Evidence for metal interaction in gold metallized polycarbonate films: An x-ray photoelectron spectroscopy investigation

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The interfacial interactions between *in situ* thermally evaporated Au and polycarbonate (PC) film, a technologically important polymeric material, is studied by x-ray photoelectron spectroscopy (XPS). Angle resolved XPS is performed to investigate the Au reactivity if any, in forming the metal-polymer interface. The spectral evidence from the above suggests that the metal interacts predominantly with the carbonyl carbon of the monomeric unit with only minor interactions with the phenyl carbons without any complex formation. In contrast to previous findings of Au to be inert at the M-polymer interfaces, this work emphasizes the salient charge transfer type interactions of Au (as electron injector) at the C=O as the primary interaction site, distributing a net charge density to C=O with the formation of a Au-CO π-back bond. The conclusions are supported by the observed new C 1s feature at 282.6 eV and the O 1s and Au $4f_{7/2}$ XPS spectral changes. The growth mode of Au on PC was proceeded by the metal monolayer deposition with cluster growth on the already weakly bonded Au onto the C=O carbon of the polymeric backbone. © *1998 American Institute of Physics.* [S0021-8979(98)09606-6]

I. INTRODUCTION

Polymers as electronic materials are increasingly used in the electronic industry. The surface modification of polymers for improvement of adhesive bonding and varying surface characteristics without concomittant modification of bulk properties has drawn extensive attention in both industrial and academic sectors. The metal polymer adhesion strongly depends on the chemical bonding at the interface and modification of surface interactions near the boundaries of confined materials can lead to new phenomena providing basis for technological applications. Therefore, the determination of interfacial bond structure and strength and interfacial morphology has been the focus of many investigations.[1–10] Recent theoretical and experimental studies have emphasized the influence of film thickness on the phase stability and studies on equilibrium properties and kinetic processes of interface materials are seeking increasing importance.

The interface structure of Cr, Ti, and Au evaporation onto Teflon-PFA, studied by XPS and mass spectroscopy (MS)[11,12] showed immediate cross linking and formation of carbide and fluoride for Cr and Ti deposition. For a less reactive noble metal as Au, only a small loss of fluorine without formation of any new species was observed. Postirradiation x-ray treatment did not promote the metal-polymer interactions for Au, Ag, and Cu, but the reactive metals (Cr, Ti, and Al) were found to react with the polymer leading to

polymer surface graphitization and an increase in the C-CF$_n$ peak intensity as a function of metal thickness. Metallization of polyethyleneterephthalate (PET) with Al, Ag, and Cu in the presence of controlled oxygen partial pressure emphasized the role of oxygen in the formation of the M-PET interface.[5] The metal at the Al-PET interface is reported to be oxidized with the formation of an oxide layer of ~ 1 nm thickness.[13]

Metallization of PC has not been studied extensively. The surface chemistry of the PC film and the adhesion of UV-cured ink has been investigated by XPS owing to its application in screen printing.[14] The degree of photo oxidation, nature of photoproduction and ink adhesion characteristics have been measured as a function of UV wavelength. Photoablation and photo-oxidative degradations in PC investigated by KrF laser ablation in air showed a linear dependence of etch data on the laser fluence.[15] The decrease of O 1s/C 1s ratio indicated the occurrence of the chain scission at the C—O bond. PC doped with hole transporting materials, e.g., styryl amine, has been used as an effective electroluminiscent material.[16] Electroluminiscence from granular Au-polymeric thin films from the Au containing polymeric layer has also been reported.[17]

The metal-polymer interfaces have been found to be nonideal implying the interface to be insensitive to the metal work function.[6] Although, the work function of Au is larger than Al, in systems such as Au-Mylar-Al, Au electrodes have injected negative charge into Mylar more readily than Al. Surface modifying factors such as line defects, thermal processing and impurities were thought to be responsible for this

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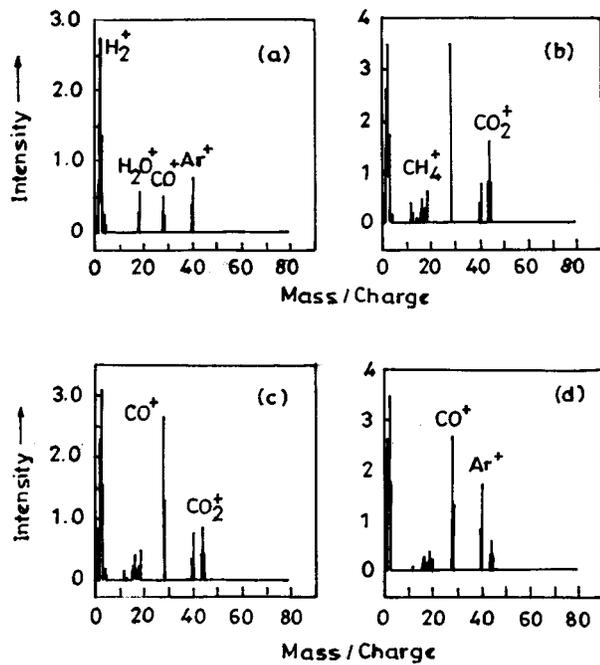
FIG. 1. Mass spectra from the XPS analysis chamber during x-ray irradiation of Au metallized PC.
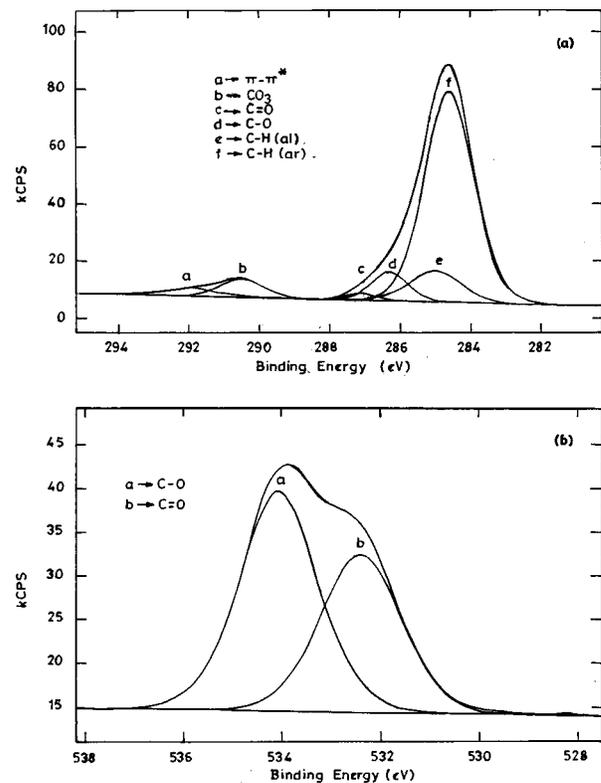

FIG. 2. (a) High resolution XPS C 1s spectrum of pristine PC film, (b) high resolution XPS O 1s spectrum of pristine PC film (the curve fitting data are shown in Table I).

enhanced negative injection. Au has also played an important role as evaporated metal electrodes (Au^-/Au^+) in conducting polymeric systems[18] and it may offer the possibility of acting as a metallic electron-injecting electrode in the fabrication of electroluminescent devices.

The use of Au as an electron injecting electrode in the possible PC based electronic devices has prompted us to investigate the Au-PC interface structure upon its formation as a function of metal thickness by XPS. Most of the previous work involving Au-polymer interfaces have focused on chemical interaction through core C 1s and Au $4f_{7/2}$ chemical shifts. This work along with C 1s features, will emphasize the possible interfacial interactions based on the core O 1s spectral changes.

II. METHODOLOGY

The PC substrates consisted of industrial films (Makrofol KG from Bayer, Germany) of thickness 15 μm. The surface contamination was eliminated by cleaning with deionized water and C_2H_5OH. The film (5×5 cm^2) was mounted on a cleaned glass slide by means of stainless steel clips. Thus, the area exposed for Au evaporation was 4.5×4.5 cm^2. The PC foil containing the glass slide was mounted in the vacuum chamber with a pressure of 2×10^{-7} Torr. At this limited pressure, build up of hydrocarbon contamination is very small since most small molecules comprising the extraneous atmosphere have a small sticking coefficient on the polymer.[19] The required amount of high purity analytical grade Au (99.999%) was placed on the crucible in the evaporation chamber and Au deposition was performed by passing the current through the electrodes attached to the crucible. The Au source and the PC substrate distance was 18.5 cm. The thickness of the deposited layers was estimated from the weight difference by a microbalance

with a sensitivity of 1 μg. A linear relationship was obtained between the metal XPS signal and the thicknesses thus inferred.

Evaporation of Au onto the PC film supported on mica and glass substrates is reported to be smooth and uniform giving rise to large, flat crystallites with pronounced {111} texture.[20] Studying the metal-polymer interactions involves monitoring the evolution of the polymer surface during the formation of the interface. It is believed that during thermal deposition of the metal, the chemical state of the surface observed at very low coverages corresponds exactly to the interface formed.[21,22] Thus, in the present study, Au thickness of 3.2 Å was chosen to be appropriate for the first monolayer interface formation on the PC film. A thicker film of 35.4 Å was coated to investigate the interface structure evolution with greater metal content.

The samples remained in the evacuated chamber after Au coating. Vacuum dessicators were used to transport the samples just before transferring them into the ultrahigh vacuum chamber. XPS measurements were made in a VG Scientific ESCALAB 210 apparatus with a Mg K_α source (1253.6 eV) operated at 15 kV and 20 mA at a pressure of $\sim 10^{-10}$ mbar. The distance between the sample and the x-ray source was 0.5 cm with an x-ray incident angle of 45° and an electron take off angle 0° with respect to normal to the sample plane with a fixed analyzer. Angle resolved experiments used electron take off angles as 40°, 70°, 80°, and 85°. The pressure during spectral acquisition rose from 10^{-10} to 10^{-9} mbar. To minimize the sample damage, acquisition

TABLE I. C 1s binding energies and % of various carbon components for the pristine PC film and for 3.2 and 35.4 Å Au-PC substrates.

Surface	Electron takeoff angle (°)	C—H (aromatic)	C—H (aliphatic)	C—O	C=O	CO_3	π-π*	New feature
		C 1s peak components, area %						
PC	0	72.0	11.0	7.3	1.4	5.1	3.1	
PC-Au (3.2 Å)	0	73.1	12.2	8.4	2.0	4.3	1.6	
PC-Au (3.2 Å)	80	70.4	11.5	3.9	4.8	3.4	0.66	4.8
PC-Au (3.2 Å)	85	53.8	9.1	4.1	2.7	1.1	0.19	29.0
PC-Au (35.4 Å)	0	74.4	9.3	7.6	4.8	3.4	0.6	
Binding energy (eV) (vide Ref. 14)		284.6	285.03	286.1	287.6	290.4	292.0	282.6

was performed with 1–2 scans. An analyzer pass energy of 100 eV with 500 meV steps was used for survey scans while, a pass energy of 20 eV with 40 meV steps was used for high resolution scans. Differential charging arising from a distribution of positive charge over the sample surface under x-ray bombardment in our experiments was compensated by doing a charge correction for signals with respect to the C 1s line at 284.6 eV as the internal standard. The extent of charging for 3.2 and 35.4 Å Au coated PC films were 2.16 and 5.12 eV, respectively.

Mass spectra of the residual gas composition in the XPS chamber were obtained with the help of a VG Scientific quadrupole mass spectrometer. The oxygen content in the XPS spectra was reduced to a few percent owing to emission of CO and CO_2 as a result of chain scission. Mass spectra up to 100 amu were recorded and Fig. 1 depicts different species formed in the XPS chamber. The major fragments in the background spectrum at 5.5×10^{-10} mbar were H_2^+, H_2O^+, CO^+, and Ar^+. With the opening of the x-ray gun, the relative intensities of the fragments H_2^+ and CO^+ increased drastically along with the evolution of CO_2. Less intense lines at m/e 12 (C_2^{++}) and 16 (O_2^{++}/CH_4^+) were also observed. In the course of x-ray irradiation, the final pressure rose to 1.2×10^{-9} mbar showing CO/C_2H_4 and CO_2 as the major volatile fragments emitted from the polymer.

III. RESULTS

The structure of the monomeric unit of polycarbonate is shown below.
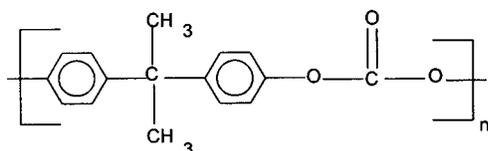
A. XPS spectra of pristine PC surface

Figures 2(a) and 2(b) show the deconvoluted C 1s and O 1s spectra of the pristine PC sample, respectively. Analy-

sis of the pristine PC spectra showed 17% O and 83% C and the chemical bonding was consistent with the chemical structure. The C 1s feature could be deconvoluted into six distinct peaks[14] (cf. Table I). The satellite peak situated at 6.1 eV below the main C 1s peak was assigned to CO_3 and the π-π* shake-up component was observed at 292 eV. The latter is associated with the presence of localized π electrons in the conjugated phenyl system. The O 1s peak positions at 532.4 and 534.06 eV, separated by $\sim$2 eV, are attributed to C=O and -O-C-O- functional groups,[14] respectively. Although stoichiometry requires the peak areas of the above two should be in the ratio 1:2, peak fitting after background subtraction shows a ratio of 1:1.35. This deviation is possibly due to the loss of oxygen during spectral acquisition.

B. Characterization of Au-PC interface

1. Comparison of C 1s, O 1s and Au 4f features with respect to Au coverage

The Au 4f, C 1s, and O 1s XPS spectra of the pristine PC sample, the 3.2 and 35.4 Å Au coated PC films are shown in Figs. 3(a), 3(b), and 3(c), respectively, at 0° electron takeoff angle with respect to the sample plane. Increasing deposition of Au caused attenuation in the C 1s and O 1s signal areas. Angle dependent XPS spectra shown in Figs. 4(a) and 4(b) for the 3.2 Å Au-PC samples show a decreasing trend in the ratio of Au $4f_{7/2}$/C 1s with a decreasing electron take-off angle. A similar trend was observed in the thicker Au-PC bilayer system implying the composition to be uniform without any contaminant. After aging the samples for $\sim$8 h in the XPS chamber, no change in the C 1s/O 1s intensity was observed indicating the metal-polymer interaction to take place during the metal deposition process.

2. The Au 4f XPS spectra

A comparison of the 3.2 and 35.4 Å Au coated PC film surfaces [Fig. 3(a)] shows the initial 84.0 eV Au $4f_{7/2}$ XPS band to shift to a lower binding energy (BE) of 83.7 eV with a narrowing of the band from 1.32 to 1.04 eV for the 35.4 Å
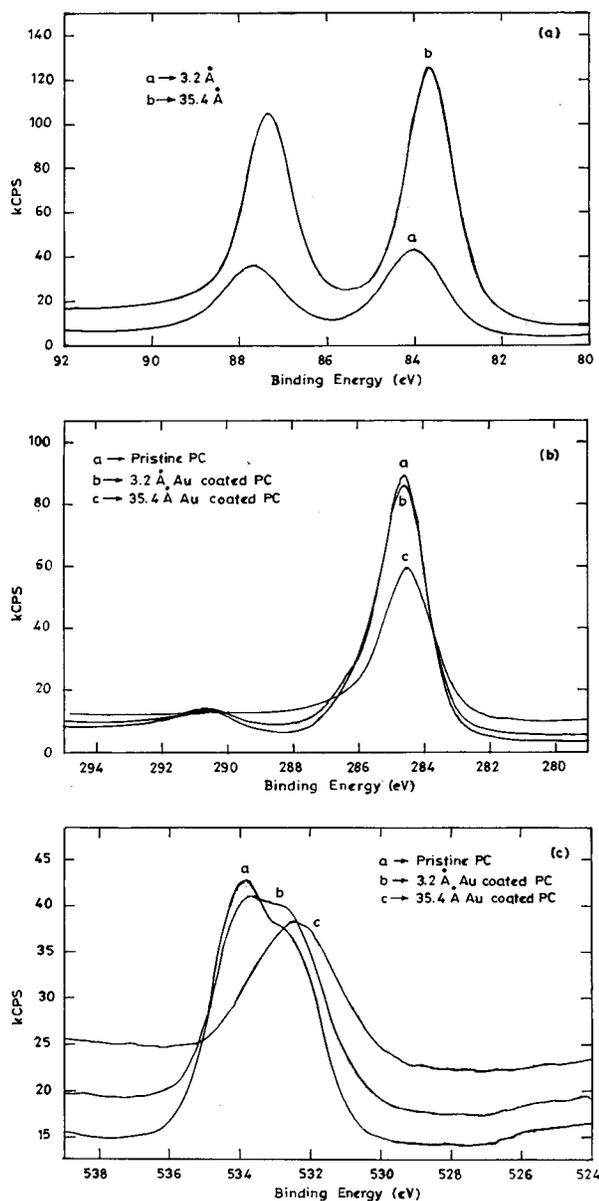
FIG. 3. Au coverage dependent (a) Au $4f$ core level, (b) C $1s$ core level, (c) O $1s$ core-level XPS spectra of PC films.

FIG. 4. Angle dependent (a) Au $4f$ and (b) C $1s$ core level XPS spectra of 3.2 Å Au coated Au-PC bilayer.

film. For angle resolved experiments, a shift of 0.6 eV was recorded. The $4f$ spin-orbit splitting remained constant within the experimental uncertainty of 0.05 eV. No new feature was observed in the Au $4f$ XPS spectra. Au primarily occurs in one oxidation state and the valence shell has a large radius. Thus the chemical shifts in the core BE are relatively small which justifies our present observation. Furthermore, since Au is a conductor and is inert to oxidation in air and has a high photoelectron cross section for the $4f$ shell, high resolution lines with BE±0.01 eV are possible for a reasonable line width of the Mg $K\alpha$ x-ray line and the spectrometer resolution.[23] The valence level spectra of the two samples were probed for both Au thicknesses; the two pronounced peaks in the valence band (VB) at 3.6 eV and 6.1 eV were attributed to Au $5d$ core levels[24] which dominated the spectra even at a low coverage (3.2 Å). A shift of 0.7 eV was
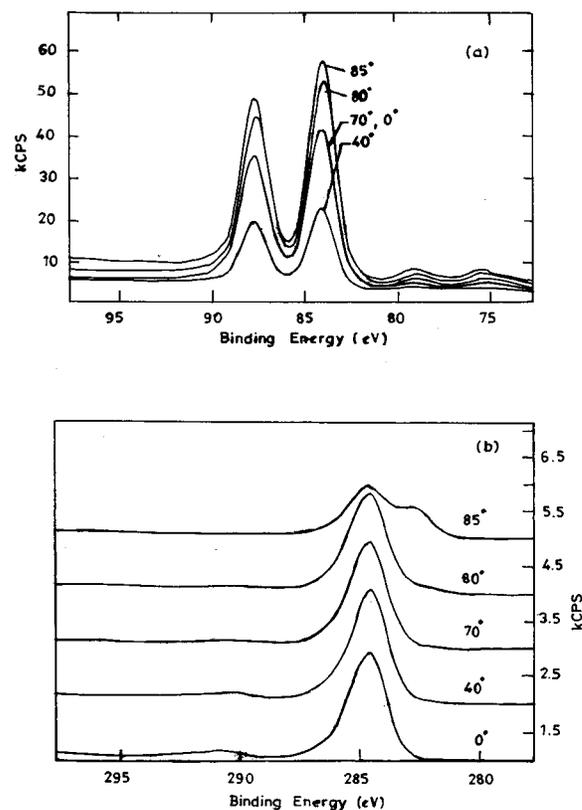
observed with the former for the 35.4 Å Au coated film. The peaks developed with respect to Au thickness, the VB broadened and both the features shifted apart.

The shifting of the metal peaks to lower BE has been explained to be due to metal cluster formation.[25] In the earlier stages of metal deposition, smaller size clusters are formed on the polymer surface. Due to a definite number of atoms in the clusters, their electronic structure represents a transitional state between the discrete energy levels of free atoms and the continuous band of bulk metals. The electronic states in the cluster are more localized than in the bulk metals which affects their electronic structure and the net effect of cluster size on the XPS BE is reported to be between 0.1 and 1.0 eV.[25] A shift of 0.3 eV in our 35.4 Å Au coated sample clearly indicates the formation of Au clusters on the polymer substrate. Charging of the metal clusters on the polymer substrate evidenced by the shift of the Au Fermi level has been studied in the case of the Au-PI system.[21] The XPS data reported a negative shift in the C $1s$ core levels of PI due to injection and trapping of photoemitted electrons from Au into the polymer. In our angle variation, experiments at 80° and 85° with 3.2 Å Au coated PC film, a new C $1s$ peak at lower BE, 282.6 eV (to be discussed in the next section), appeared which perhaps is due to the Au-C charge transfer interaction through charge trapping at C with the formation of negative carbons.[4] However, these interactions could not be detectable from the core Au $4f_{7/2}$ spectra which is in agreement with previous reports.[26] Furthermore, at high coverage, this interaction showed no finger print. Earlier
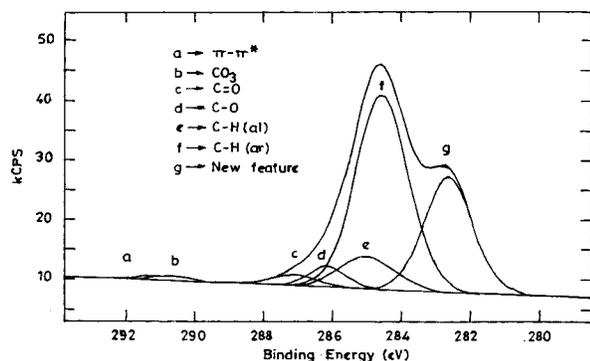
FIG. 5. C 1s core-level XPS spectrum of Au-PC (3.2 Å) film at 85° electron takeoff angle.

TABLE II. O 1s binding energies and % of various oxygen components for the pristine PC film and for 3.2 and 35.4 Å Au-PC substrates.

Surface	Electron take-off angle (°)	C=O	C—O	New feature	
	O 1s peak components, area %				
PC	0	42.0	58.0		
PC-Au (3.2 Å)	0	38.8	43.3		
PC-Au (3.2 Å)	80	40.5	36.7	5.1	
PC-Au (3.2 Å)	85	32.8	23.3	21.9	4.2
PC-Au (35.4 Å)	0	34.6	35.9		
Binding energy (eV)		532.4	534.0	530.1	527.9

The C=O and C—O % for Au coated samples are not calculated with respect to 100% O, but with respect to the total oxygen after depletion upon x-ray irradiation.

3. C 1s spectra

The C 1s shake-up satellite component at 292.0 eV decreased sharply in intensity [Fig. 3(b)] as a function of Au thickness suggesting a weak interaction between Au and the π-conjugated electrons of the phenyl ring. Since the shake-up structure are the characteristics of higher occupied and lower unoccupied valence orbitals, the shake-up satellite feature is very distinct originating from the π-π^* transitions of the unsaturated backbone, accompanying core ionization. The relative variation in the intensities of this feature for the Au-PC substrates therefore indicates different modes of Au interaction with PC. Since the 290.4 eV C 1s feature is assigned to the CO_3 group, a reduced intensity may also imply C—O bond breaking due to chain scission, preceeding the destruction of the CO_3 group due to radiation damage. However, this effect is negligible and may be considered in reference to the total oxygen content associated with the pristine PC and the two Au coated samples which were reduced from 17% to 14% to 12%, respectively.

The absence of any new C 1s feature at 0° electron take off angle for the samples essentially indicates no strong metal interaction with the polymeric backbone. However, our angle resolved experiments at 80° showed the appearance of a new peak (g) at 282.6 eV with a negative shift of the C 1s for the 3.2 Å coated film. The intensity of this peak increased from 4.8% to 29% at 85° (Fig. 5). No such feature could be seen to exist for the 35.4 Å film. Polzonetti et al.[4] have reported a similar C 1s feature at 282.5 eV in the Cr-PI system whose intensity was seen to increase with metal coverage. The phenomena were related to the growth mode of Cr and to the strong interaction between the metal atoms and the C=C chain units of the phenyl ring of the polymer and to the formation of negative carbon. The present observation of the negative shift of the C 1s level is possibly a result of weak Au→C=O charge transfer type interaction. However, a similar signature in the Au 4f XPS spectra is not observed. This result is however, in agreement with literature data,[26] which state that for metal-polymer interfaces, charge transfer

interactions are hardly detectable at the metal core level XPS spectra.

Almost all previous work on Au-polymer interfaces have reported them as nonmetallized surfaces. The difference between the noble and the reactive metal-polymer interfaces are described not to be related to metal complexes but to the (i) entrapment of fragments from polymer chain scission near the interface or in the metal film and to the (ii) recombination reactions of radicals produced during metal deposition as a result of bond breaking. These reactions are limited by the mobility of the radicals and steric hindrance. Radicals in the near proximity react with the others chemisorbed in the metal film or at the near surface. The bond breaking and hence the concentration of radicals created increased with metal reactivity and thickness.[12] With Al, the interface on PET film is reported to be formed with the formation of organometallic complexes of the type Al-O-C through Al grafting.[5] The complex formation pathway followed a chemical attack on the carboxylic groups of the PET polymer but with Ag and Cu as much less reactive metals, a reaction mechanism involving metal diffusion into the free volume of the polymer is reported by these workers. The origin of bonding at these diffusive interfaces has been explained through charge transfer complexes or pure physical adhesion which has been invoked.

4. O 1s spectra

Figure 3(c) shows the O 1s core level XPS spectra for the pristine, the 3.2 Å, and the 35.4 Å Au coated PC films. Spectral deconvolution and fitting results are included in Table II. Although no new feature was observed at 0° electron take-off angle, large chemical shifts and changes in the peak areas of C=O and C—O O 1s signals were seen. For the 35.4 Å Au-PC substrate, shifts of 0.45 and 1.1 eV for C=O and C—O peaks, respectively, towards lower BE were encountered. The O 1s (C—O/C=O) area ratio decreased in the order 1.41−1.11−1.03 for the pristine and the 3.2 and
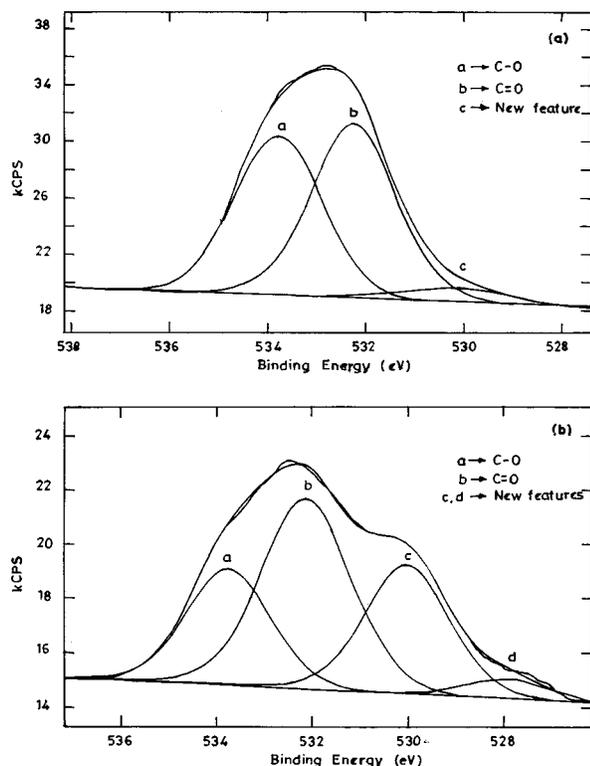
FIG. 6. O 1s core-level XPS spectrum of Au-PC (3.2 Å) film at 80° electron takeoff angle; (b) O 1s core-level XPS spectrum of Au-PC (3.2 Å) film at 85° electron takeoff angle.

35.4 Å samples, respectively, with a total oxygen atomic percent reduction from 17% to 14% to 12% for the same sample sequence.

The detailed angle resolved XPS data for O 1s signals are reported in Table II. For the 80° electron take-off angle, the O 1s component corresponding to single bonded oxygen in 3.2 Å Au coated PC film decreased markedly from an initial value of 58% to 36.7%, while a new lower BE component formed at 530.1 eV [Fig. 6(a)] representing an area of 5.1% of the total oxygen. This feature cannot be concretely attributed to Au-O bonding since a corresponding feature did not arise in the Au 4$f_{7/2}$ XPS spectrum. Figure 6(b) shows the O 1s spectral behavior for the same sample at the 85° electron take-off angle. Along with a reduction in the C—O component, the C=O component also decreased drastically from 42% to 32.8% with the appearance of a second new peak at a lower BE of 527.9 eV which represented an area of 4.2% of the total oxygen.

The O 1s spectral changes could be interpreted in terms of Au interacting with the C=O group of the polymer and donating electron density to the same. This phenomena is well evidenced in the shifts of C=O and C—O O 1s signals to lower BEs resulting in new features. As Au thickness varied and the Au overlayer grew (35.4 Å), no new features were observed in the O 1s XPS spectra even though C—O and C=O intensities decreased substantially. Since Au clusters are formed through agglomeration/condensation at greater metallization, the system overlayer composition and morphology are perhaps controlled by the compositional changes in the 1–2 top monolayers on the substrate. Inter-

face chemistry of Mg-PET through O 1s spectral changes indicated Mg to adsorb on the polymer surface via the addition reaction with the C=O group with the formation of Mg—O and Mg—C bonds.[27] In the case of Mg metallization for longer time intervals, metallic cluster formation by Mg adsorption onto the initial Mg at the interface is reported without any O 1s spectral shifts or appearance of new peaks, strongly supporting our observation.

IV. DISCUSSION

The C 1s XPS signals in the study of interface chemistry of Au metallization onto PC implied a weak interaction with the phenyl carbons as evidenced from the intensity changes of the π-π^* transition signals and the appearance of the 282.6 eV C 1s feature in the angle resolved XPS spectra, attributed to Au→C=O interaction. It is concluded that in the presence of a more reactive group like C=O, the aromatic sites are not preferable for metal interaction, but the delocalized phenyl electrons are sensitive to any variation of the electronic structure at the metal-polymer interface as observed from the intensity changes of the π-π^* peaks. The pronounced chemical shifts in C—O and C=O groups clearly indicate that the Au→C=O interaction occurs after the formation of the first monolayer Au-PC interface corresponding to 3.2 Å Au metallization. In the interaction between Au and C=O, a net donation from Au (valence ''d'' orbitals) to CO takes place. The CO group has vacant π orbitals in addition to lone pairs. These vacant orbitals accept electron density from the Au filled orbitals to form a type of π bonding (π-back bonding) that supplements the σ bonding arising from lone pair donation. High electron density on Au is thus delocalized onto the low-lying π orbitals of CO. As the extent of the back donation from Au to CO increases, the Au—C bond becomes stronger and the C=O weaker.[28] As a consequence of losses in the d-electron population, the Au 5d bands (3/2 and 5/2) in our experiments showed higher BE shifts for the 3.2 Å film as compared to the 35.4 Å substrate. For higher metallized PC films, as in the case of the latter, the Au cluster formation is possibly hindering the back donation of charge density to C thus, resulting in no new (282.6 eV) feature in the C 1s XPS spectrum. The physical evidence for the multiple nature of Au—CO bonds are perhaps reflected in the appearance of new C 1s band and shifts in the C=O and C—O to give rise to new features at 530.1 eV and 527.9 eV with a substantial at. % of 21.9 and 4.2, respectively. Similar interactions have been studied in metal carbonyls[29] where the net effect was evaluated for σ donation of the CO ligand and the back donation from the metal ion. The C 1s, O 1s and the metal core XPS BEs confirmed that a net donation from the metal to the ligand takes place. The results have been found to tally with the MO calculations.

Based on the above findings, an interaction scheme is proposed in Fig. 7 which shows the formation of a π back bond between Au and CO followed by a Au attack onto the C=O carbon as the primary interaction site [Fig. 7(b)]. The formation of this Au→CO π-back bond can result from the dative overlap of a filled $d\pi$ or hybrid $dp\pi$ Au orbital with
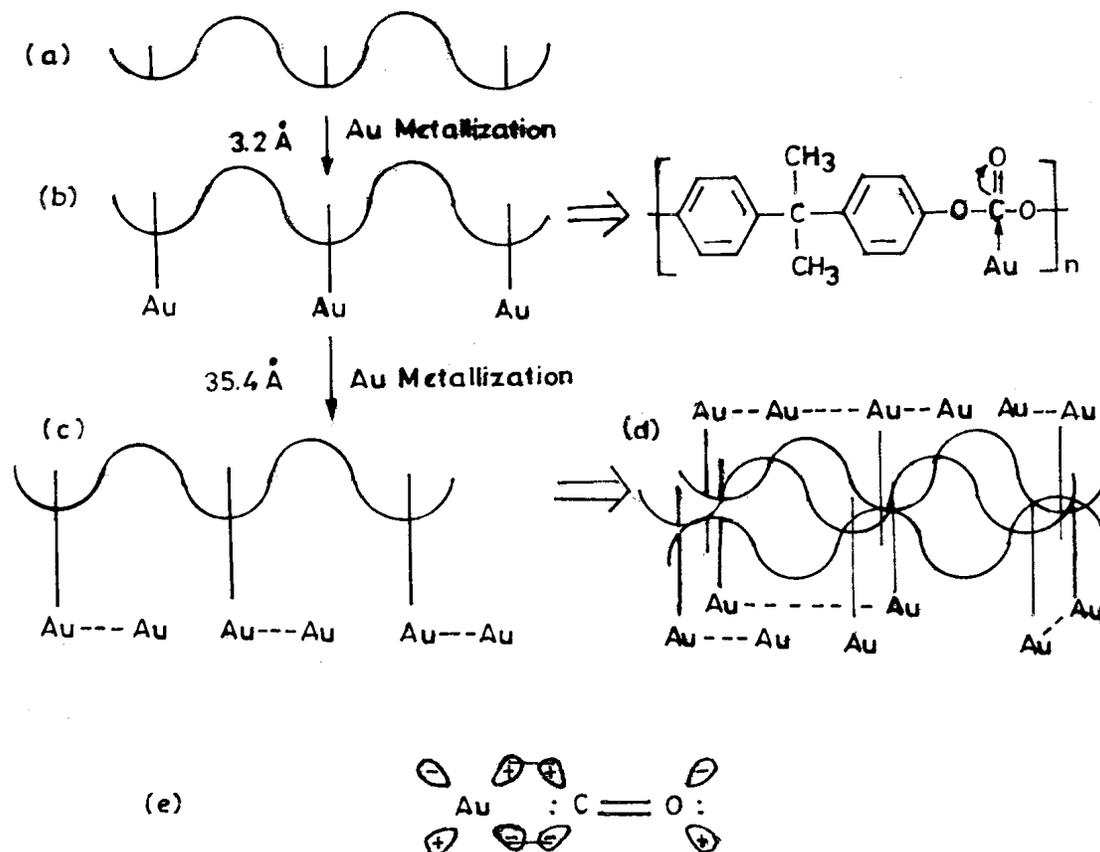
FIG. 7. Probable scheme for interactions at the Au-PC interface and at greater metallization of the PC surface. (a) The monomeric unit of PC with C=O groups protruding upwards; (b) Au-C back π bond formation at the C=O site in the monomeric unit; (c) Au cluster formation on the already weakly bound Au to carbon on the monomeric unit; (d) intra/inter Au-PC interactions; intra–Au-Au interaction in the same PC monomeric unit; inter–Au-Au interactions between different monomeric units; (e) formation of Au–CO π back bond.

an empty anti-bonding $p\pi$ orbital of the CO group[31] [Fig. 7(e)]. Infrared spectral studies on Cr and Cu metallization of PET and PI[8] support the observation of metal-carbon bonding and models have been proposed by Wong et al.[26] for the Mg-PET interface. The latter have reported Mg—O and Mg—C bond formation supplemented by XPS observations. Figure 7(c) depicts the building up of large size Au clusters on the weakly bonded Au at the Au-PC interface. In Fig. 7(d), intra- and intermolecular metal-polymer and metal-metal cluster interactions are shown in the same and between different monomeric units present within the Au interaction zone on the polymer surface. Atomic Au has a $5d^{10}6s^1$ electronic configuration. The interaction between Au–Au of different monomeric units according to Fig. 7(d) can exist as a weak Au($5d$)$\rightarrow$Au($6s,6p$) rehybridization.[30, 31]

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