Application of Variable-Temperature Ellipsometry to Plasma Polymers: The Effect of Addition of 1,7-Octadiene to Plasma Deposits of Acrylic Acid

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Introduction

Plasma polymers are scientifically interesting and commercially important materials, with realized applications in a diverse range of technologies.[1] Highly functionalized plasma polymers may be deposited at low plasma input power.[2] Applied as thin-film coatings to commodity materials, plasma polymers can substantially add value. Plasma polymerization offers significant advantages over other surface-modification technologies, namely the production of ultrathin pinhole-free coatings, control over film thickness and chemistries, and the ability to conformally coat objects of complicated geometry. Plasma polymerization is also a potential route to new materials that are not accessible by other means.

However, the thin-film nature of functionalized plasma polymer films has seriously restricted their analysis by conventional analytical techniques (e.g., nuclear magnetic resonance, gel permeation chromatography, etc.). Hence, in some important respects these materials remain poorly defined. While, X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), and reflectance-based infrared spectroscopes (IR) have all provided useful valuable insights into the chemical nature (e.g., functional group composition) of these materials, the network characteristics of these materials (e.g., cross-link density, sol-content) are more difficult to explore.

Here, we report for the first time, on the application of variable-temperature ellipsometry (VTE) to measure the sol fractions in functionalized plasma polymers and plasma copolymers of acrylic acid (AA) and 1,7-octadiene (OD). Sol fraction is defined as the fraction of soluble molecules, i.e., unreacted monomers and oligomers which are not bound to the network. Elsewhere, the uses of plasma copolymers of AA/OD as adhesion promotes and as cell culture surfaces are described.[3] A comprehensive effort to probe the physical properties of these plasma copolymers, by extraction with various solvents has been reported.[4] However, this approach can only yield indirect information, from which the network characteristics of the deposits are inferred (e.g., percent sol fraction).

Experimental Methods

VTE. A commercial ellipsometer has been equipped with an oven. Control over temperature during ellipsometric measurements and subsequent data analyses are performed automatically. Details of the experimental setup and errors of the method are described elsewhere.[5]

Plasma Polymerization. Silicon wafer substrates were placed in a tubular glass reactor evacuated by a two stage rotary pump. The plasma was sustained by a radio frequency (RF) signal generator and amplifier inductively coupled to the reactor vessel. For more details on the reactor design see ref 3. AA was allowed to flow through the reactor via a needle valve, and copolymers were deposited with 0%, 25%, 50%, 75%, and 100% OD. AA and OD were copolymerized at a plasma power of 2 W and a total flow rate of 2.0 sccm (the pressure in the reactor was $\sim 4 \times 10^{-2}$ mbar). For all copolymerizations, a deposition time of 120 min was used. The monomer mixtures were allowed to flow for a further 20 min after the plasma was switched off to minimize the up-take of atmospheric oxygen by the deposits. OD was polymerized for 60 min, at 3 W.

XPS analyses were undertaken on a VG CLAM 2 XPS.

Results and Discussion

Plasma copolymerization of AA with OD can be used to prepare films containing different concentrations of carboxyl group. The quantified XPS data obtained from plasma copolymerizations of AA with 0%, 25%, 50%, 75%, and 100% OD are presented in Table 1. From the table it can be seen that the relationship between the molar fraction of AA in the plasma gas and the carboxyl group concentration in the deposit is not linear. A linear relationship should not be expected. In AA there are three carbons (one of which is a carboxyl) in OD there are eight carbons. In the deposit we count the total number of carboxyl groups per 100 carbons, irrespective of whether they came from AA or OD. Furthermore, the deposition rates (nm/min) of the two compounds (in their pure state) is known to be different, 2.6 nm/min for AA and 8.6 nm/min for OD (under the described conditions). The addition of 25% OD reduces the surface O/C and carboxyl group concentration by just over 50%.

In Figure 1, the changes in relative thicknesses (d_{rel}) of the plasma polymers and copolymers of AA and OD

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Table 1. Quantified XPS Data from Copolymerizations of AA/OD

molar ratio AA:OD	O/C ratio	composition of C 1s core line (%)				
		C—C/H	C—COOR	C—OH	C=O	COOR
100:0	0.52	48.9	22.5	4.1	2.4	22.5
75:25	0.24	75.4	9.1	5.3	1.0	9.1
50:50	0.19	80.2	4.8	8.9	1.8	4.8
25:75	0.12	86.5	1.8	7.8	2.1	1.8
0:100	0.08	93.0		7.0		

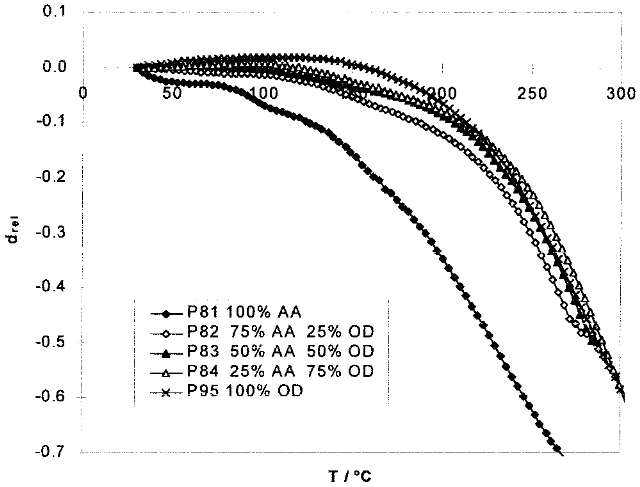

Figure 1. Film thickness (d_{rel}) versus temperature (T, °C) for plasma polymers of AA and OD and plasma copolymers AA and OD.

are shown over the temperature range 30−300 °C. It is evident from this graph that in the temperature range 30−100 °C only the film thickness of the plasma polymer of AA is changing significantly. This is attributed to mass loss occurring in this sample. The plasma copolymers of AA and OD, prepared using 25%, 50%, and 75% OD, respectively, and the plasma polymer of OD show much more stable behavior over this temperature range. Any small mass losses in these samples are more or less balanced by any increases in film thicknesses arising from thermal expansion.[6] The error in d_{rel} is temperature dependent[5] and at 30 °C is, by definition 0, and at 150 °C it is 0.004. Therefore, it appears that the small differences seen between the plasma copolymers are outside the measurement error. The large change seen in the plasma polymer of AA is attributed to the loss of absorbed water, nonbound AA and other (similarly) nonbound volatile materials. Figure 1 clearly shows that the addition of 25% OD (to the AA plasma gas) is enough to sufficiently cross-link the plasma copolymer films, to significantly reduce outgassing of nonbound material. This simple experiment elegantly demonstrates the insight afforded by VTE: Previously, we had attempted to qualitatively assess the cross-linking potential of OD on the basis of a series of extensive and time-consuming XPS−water solubility experiments.[7] From washing plasma copolymers in distilled water it appeared that the addition of somewhere in the region of 20−30% OD (to an AA plasma) was required to stabilize the plasma copolymer product to dissolution. However, the interpretation of the data was complicated by possible reactions of the plasma copolymer surface with water.

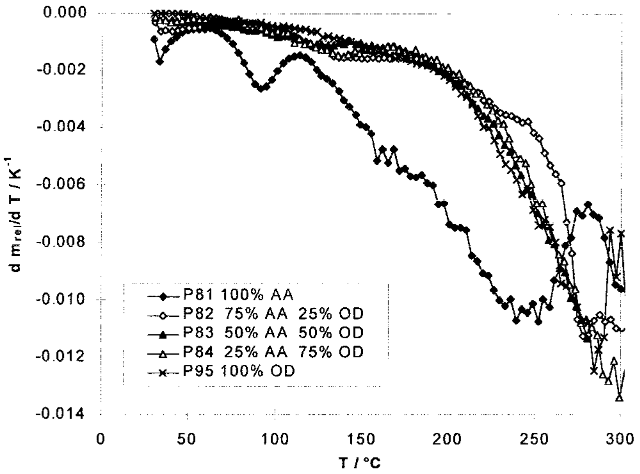

Figure 2. Comparison of mass loss rate over temperature for plasma polymers with different ratios of AA and OD.

Above 100 °C, significant decreases in d_{rel} are observed in all the plasma deposits, but these are still most marked in the plasma polymer of AA. It is not immediately clear from the data as to whether these changes are occurring as a result of volatilization of entrapped material from the plasma deposits, or through thermal decomposition. The lower cross-link density in the AA plasma polymer deposit may negatively impact upon its thermal stability. It is possible that the loss of volatile components (sol) and thermal degradation overlap in this temperature range. To separate the kinetics in the case of such overlapping processes, a combination of VTE and mass spectroscopy has to be used. This is the subject of current work. In the plasma copolymers of AA and OD and the plasma polymer of OD, the thinning process becomes marked above 150 °C. By 300 °C, the plasma copolymers and plasma polymer of OD have reduced in d_{rel} by 80%. The response in these films is remarkably similar. This indicates that changes in the physical structure of these plasma deposits are not (linearly) in proportion to the addition of OD.

The “onset” temperatures for the various processes in these films are better seen when the rate of change in mass (dm/dT) is plotted versus temperature (T), as in Figure 2. The mass of the coating can be calculated from the sample refractive index and the sample thickness. The refractive index is converted to density using the Lorenz−Lorentz relation.[5] This conversion is appropriate as long as no significant chemical changes occur in the material over the temperature range being investigated. In the plasma polymer of AA, it can be seen that there are two distinct mass loss events with maximum rates (i.e., minimums in Figure 2) at 30 and 90 °C, respectively. The first event is attributed to the evaporation of water; the second peak is presumed to be the volatilization of entrapped AA and possibly volatile, higher mass components (oligomers). Water uptake in plasma polymers of AA has been measured using a quartz mass balance.[4] Uptake occurs on letting-up the plasma reactor to atmosphere. Water uptake is reported to be reversible and to be as much as 4% (by weight, 30% RHH).[4] The boiling point of AA is 141 °C; in thin films, outgassing of entrapped AA would been seen well below this temperature. Loss of carboxyl

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(6) d_{rel} is calculated from the error in CTE (~20 × 10^{-6}/°C).

(7) Daw, R.; Candan, S.; Beck A. J.; Devlin, A. J.; Brook, I. M.; MacNeil.; Dawson R.; Short R. D. *Biomaterials* **1999**, *19*, 17.

groups is reported on the long-term storage of plasma polymers of AA.[4] An aroma, similar to that of acetic acid, is reported which suggests an acidic compoenent is being lost.[4] Further, washing with hexane (a nonpolar solvent) reduces the measured carboxyl concentration.[4] The second peak may also account for the outgassing of higher molecular weight volatiles.[8] It should be noted that all of these assignments are speculative and require confirmation. No distinct mass loss events are seen in the plasma copolymers, indicating a much lower sol content. The significantly greater rate of mass loss in the plasmer polymer of AA above 100 °C suggests reduced thermal stability (cf. the plasma copolymers) or the continued outgassing of higher molecular weight volatiles.

In conclusion, VTE is shown to be a powerful technique for probing thin-film plasma polymers. Herein, we have shown how the relative sol fractions of plasma polymers/copolymers can be measured, as can their thermal stability. VTE can further provide the refractive indices of these films and their coefficients of thermal expansion (CTE). By coupling VTE with a mass spectrometer a fuller understanding of the fractional nature of these low power plasma deposits ought to be achieved.

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