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Effects of Aging on Chlorinated Plasma Polymers

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Thin films deposited from propanol-chloroform-argon mixtures by plasma enhanced chemical vapor deposition at different partial pressures of chloroform in the feed, C_{Cl}, were characterized after two years of aging and their characteristics compared with their as-deposited properties. Film thickness decreased and surface roughness increased with aging. Surface contact angles also increased with aging for the chlorinated films. For the film deposited with 40% chloroform in the feed the contact angle increased about 14°. Transmission infrared and Energy dispersive X-ray spectroscopy revealed that the films gain carbonyl and hydroxyl groups and lose chlorine and hydrogen on aging. Chlorination appears to make the films more durable. Delamination was observed for the unchlorinated films.

Keywords: *thin films; a-C:H:O:Cl; IRS; stability; contact angle*

1. Introduction

Although some studies have been made on amorphous hydrogenated carbon films containing chlorine[1-3] there is still a relative dearth of literature dealing with such materials. Here, a-C:H:O:Cl films deposited from plasmas fed propanol, chloroform and argon[1] and aged for two years are characterized to investigate any morphological, structural and compositional changes.

In the present investigation, film thickness and surface roughness were studied using Profilometry. Surface contact angles were measured using goniometry. Chemical structure and composition are examined using Transmission infrared spectroscopy and Energy dispersive X-ray spectroscopy, respectively. Surface features of the aged films were examined using Scanning electron microscopy.

2. Experimental

2.1 Film Production

Details of the depositions are given in the literature[1]. In brief, films were produced by the PECVD of propanol-chloroform-argon mixtures at constant total pressure, and partial pressures of chloroform of 0 to 40%. As the proportion of chloroform in the feed was increased the proportion of argon was correspondingly decreased.

2.2 Characterizations

Film thickness was measured using a profilometer on samples deposited onto smooth glass plates containing a film step-height delineated during the deposition process with the aid of a mask. Nine horizontal scans of 2000 μm length obtained with a Veeco Dektak 150 profilometer were taken. Surface roughness, R_a, was calculated from these data for each film.

Surface wettability was determined from contact angle (θ) data taken using a Ramé-Hart 100 goniometer. These measurements were conducted immediately after deposition and two years later. The samples were stored for ageing under ambient atmospheric conditions for two years. Three drops of deionized water (0.2 μL) were deposited on different regions of the sample surface and the contact angle was measured 10 times on each side of the drop, resulting in sixty θ values per sample.

A Jasco FTIR-410 spectrophotometer was used for transmission infrared spectroscopy in the 4000 to 400 cm^{-1} range. Each spectrum comprised 128 scans; a resolution of 4 cm^{-1} was achieved.

Images of the aged films were obtained using a Jeol JSM-6010LA scanning electron microscope equipped with a secondary electron detector. Chemical composition of the aged films was studied using EDS.

3. Results and Discussion

Figure 1 shows the film thickness as a function of the percentage of chloroform in the feed, C_{Cl}. The aged films tend to be thinner perhaps owing to the loss of chlorine as discussed below. Decreases of around 10% have been observed in the aging (-40 days) of a-C:H:O films (where a-prefix indicates

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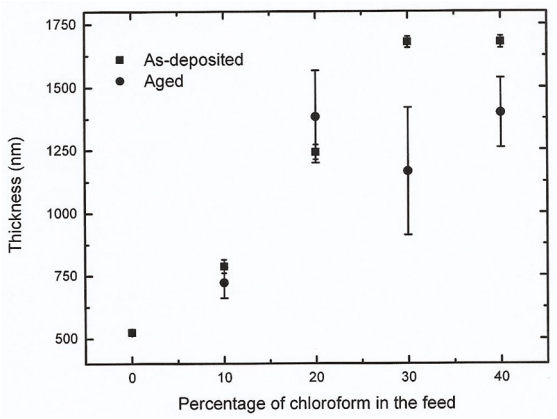

Figure 1: Film thickness as a function of C_{Cl} for the as-deposited and aged films.

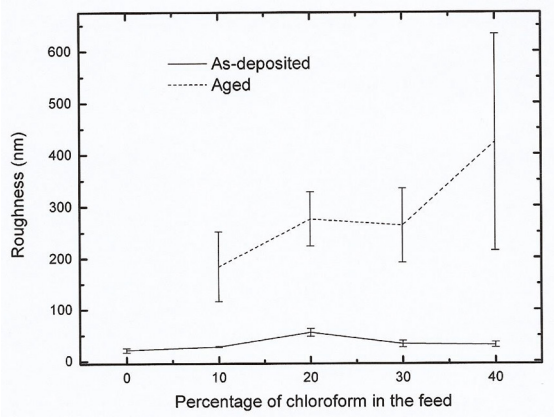

Figure 2: Surface roughness as a function of C_{Cl} for the as-deposited and aged films.

amorphous) produced from acetone plasmas[4]. Apart for the absence of chlorine, these films have chemical compositions similar to the films examined in the present study. For the most chlorinated films in the present study, which were obtained at C_{Cl} of 30% and 40%, the relative thickness decreases were roughly 30% and 13%, respectively. The condition of the aged unchlorinated film prevented its thickness from being reliably measured. However, the film deposited at C_{Cl} = 10%, and therefore having very low chlorine content, suffered a decrease in thickness of around 8%, compatible with the value of 10% cited above for a-C:H:O films.

Figure 2 shows the surface roughness, R_a, as a function of C_{Cl}. The aged films are consistently and considerable rougher than the as-deposited material, R_a increasing from around 50 nm to more than 200 nm for the aged films. This may be due to the strong de-chlorination and increase in oxygen-containing functionalities as revealed by the infrared and elemental analyses discussed below. (The roughness of the unchlorinated film could not be reliably measured.)

Figure 3 shows the surface contact angle as a function of C_{Cl}. There is a clear tendency to greater contact angles with aging for the originally more chlorinated films. For the film deposited at a C_{Cl} of 40%, the surface contact angle increases from ~72° to ~86°. The increase in the presence of polar oxygen-containing groups with aging would be expected to decrease the contact angle but the considerable increase in roughness (Figure 2) tends to increase it. The magnitude of the contact angle is similar to those obtained for a-C:H:Cl films containing considerably more chlorine (~45 at.%), for which the contact angles were about 77° [2].

Figure 4 shows transmittance spectra of pairs of films (as-deposited and aged) produced at C_{Cl} (percentage of chloroform in the feed) of 0, 10, 20, 30 and 40. All spectra show absorptions at 2950, 2900 and 2850 cm^{-1}, respectively, due to CH, CH_2 and CH_3. Similarly, owing to CH_2 and CH_3 groups, all the spectra show absorptions centered around

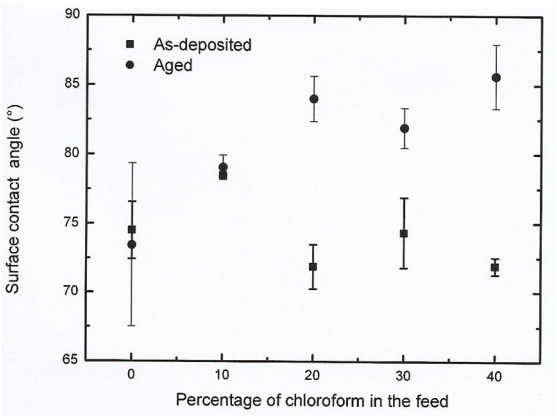

Figure 3: Surface contact angle as a function of C_{Cl} for the as-deposited and aged films.

1450 and 1380 cm^{-1}. All spectra also exhibit a characteristic absorption at around 1700 cm^{-1}, attributed to the presence of stretching in C=O groups. Inspection of Figure 4 reveals that the peak heights of the absorptions due to C=O increase in the aged films compared to the peaks due to CH_x.

The spectra of the aged chlorinated films show a clear absorption at ~1080 cm^{-1} due to –C-O groups in a primary alcohol. The peak heights of the –C-O absorption tend to increase compared to those due to CH_x as the proportion of chloroform in the feed increases.

An absorption at ~3500 cm^{-1}, attributed to the presence of hydroxyl groups, increases as C_{Cl} increases, and also tends to be greater for the aged sample in each sample pair.

Aging causes the incorporation of oxygen as C-O and C=O, and also of OH groups. This is typical of plasma polymers, which on deposition usually have a high density of free-radicals that react with oxygen and water vapor[5, 6] when exposed to ambient conditions. Thus carbonyl and hydroxyl groups are produced[7]. Although this process can

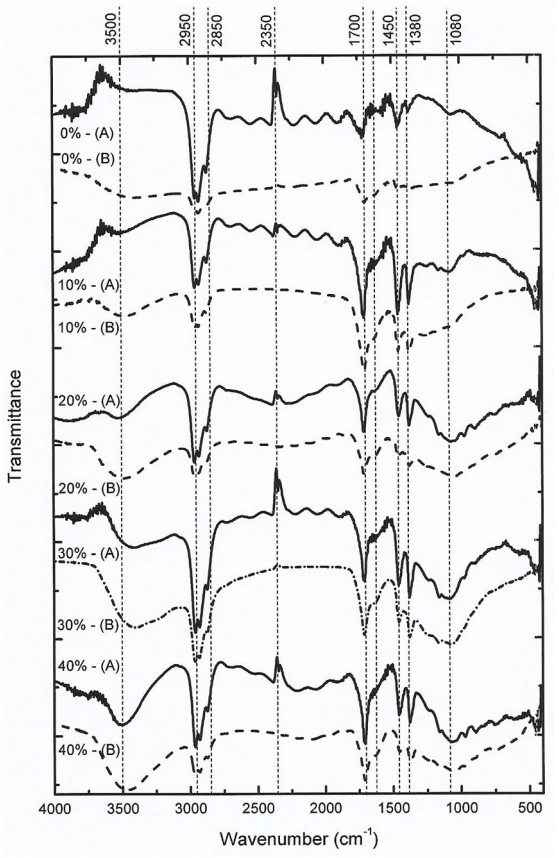

Figure 4: Transmission infrared spectra in the 400 to 4000 cm^{-1} range of pairs of films, (A) as-deposited, (B) aged, as a function of C_{Cl}.

occur in seconds, it can apparently also continue slowly thereafter on a scale of months or years.

A shoulder to the lower frequency side of the 1700 cm^{-1} peak (at ~1650 cm^{-1}) is more clearly visible in the aged films, and is attributed to the presence of C=C bonds, which are not present in molecules of the monomers or comonomers (propanol and chloroform). These likely result from dehydrochlorination, which is known to occur in the aging of conventional poly(vinyl) chloride[8].

Table 1 shows the elemental compositions (C, O, Si and Cl) of the original and aged films as determined by XPS and EDS, respectively. The latter analyses are more characteristic of the bulk compositions. The concentration of oxygen at the surface of the original films is typically higher than in the bulk. Hence the lower concentrations registered for oxygen of the aged films reflect this fact. The infrared spectra discussed above indicate a relative increase in oxygen-containing functionalities upon aging. Chlorine, which is dispersed in the bulk, is clearly lost with aging.

The aged unchlorinated film showed signs of delamination and appeared to dissolve when exposed to water droplets. A tiny contamination with Si, possibly present in the substrate, was observed for this film.

Scanning electron micrographs of the aged films are shown in Figure 5 (a to e). The surface of the aged film deposited without chloroform (Figure 5a) appears irregular and particulate material is present. In Figure 5c spherical particulate matter with a range of diameters of 1 μm or less is observed. On the same scale the films grown at the highest C_{Cl} (Figures. 5d and 5e) appear more uniform. Visually the unchlorinated film showed some delamination and the more chlorinated films a more uniform coverage.

4. Conclusions

On aging over two years under ambient conditions, chlorinated amorphous plasma films are oxidized, possess greater densities of OH, C-O, C=O and C=C bonds, and suffer dehydrochlorination. In addition, film thickness decreases while surface roughness and the surface contact angle increases. The chlorinated films tend to be more stable, resistant to delamination, and present a more uniform aspect in electron microscopy images.

5. Acknowledgements

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Table 1. Elemental composition (at.%) as a function of C_{Cl}, the percentage of chloroform in the feed, for the as-deposited and aged films. Data for as-deposited films were previously published in ref[1].

Element	C		O		Si		Cl	
C_{Cl} (%)	As-deposited	Aged	As-deposited	Aged	As-deposited	Aged	As-deposited	Aged
0	88.7	90.4	11.3	8.1	--	1.3	-	-
10	82.2	90.6	11.1	9.1	--	0.04	2.7	0.3
20	81.4	88.9	12.4	10.1	--	--	6.3	1.0
30	80.2	88.9	12.2	8.4	--	--	7.6	2.7
40	80.0	91.7	12.3	8.2	--	--	7.7	0.2

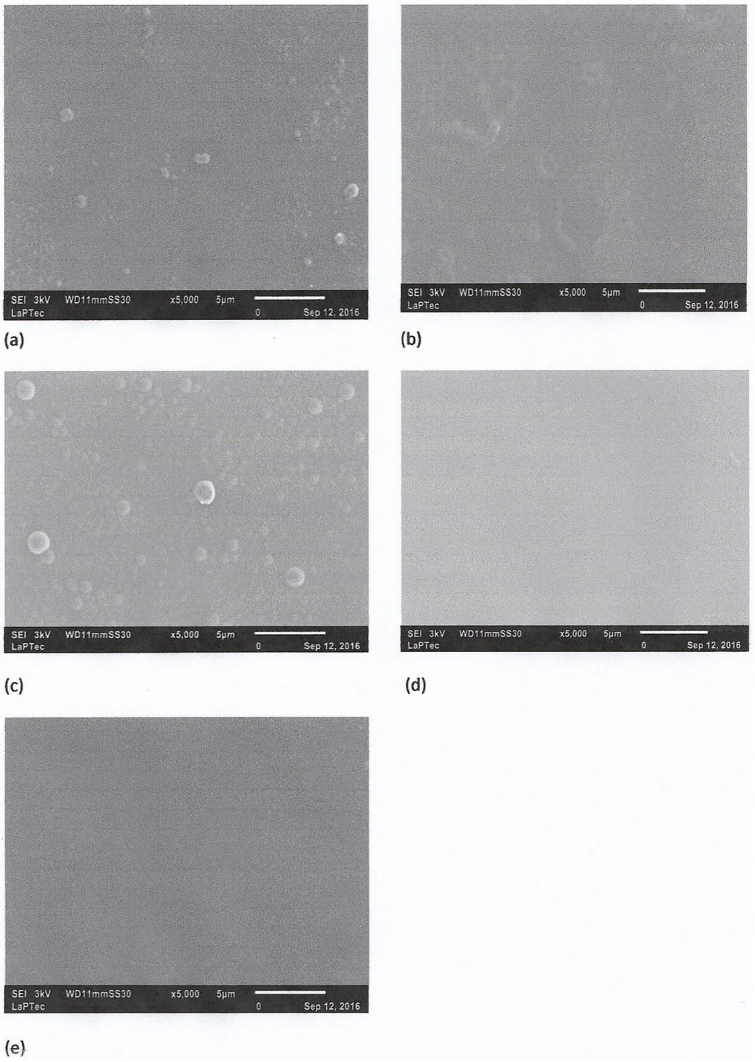

Figure 5: Scanning electron microscopy images of the aged films at C_{Cl} values of (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40%.

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