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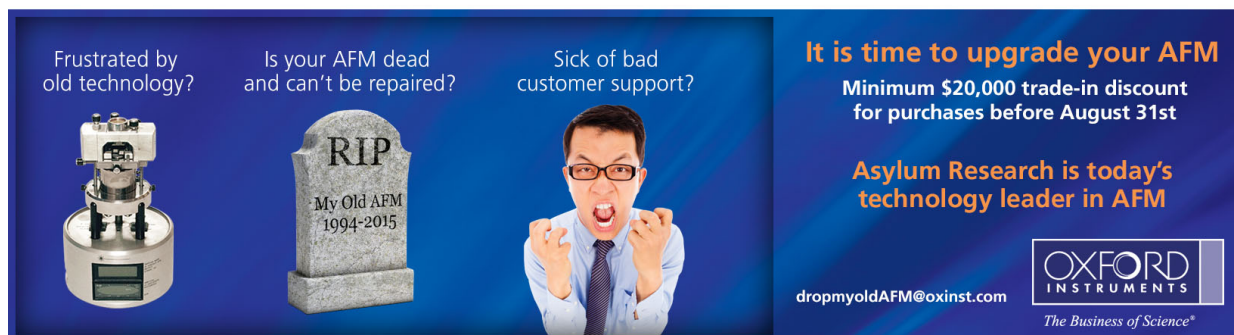J. Appl. Phys. **59**, 2977 (1986); 10.1063/1.336912

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Time evolution of the residual stress of plasma-polymerized acetylene films in various ambients

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The behavior of the residual stress with time of plasma-polymerized acetylene films in various ambients has been investigated. The plasma polymers were deposited on thin glass substrates in dc and rf discharges of acetylene. After deposition, the specimens were mounted in a chamber that could be evacuated or filled with air, oxygen, or nitrogen. Stress measurements were carried out by the bending beam method, using a He-Ne laser. A steady rise in the stress during time periods of several hours following film deposition was observed in most of the samples studied. Stress increments of more than one order of magnitude were detected in some of the films upon exposure to air. Pronounced stress increments were also observed during exposure to oxygen. Rises in the stress were detected even in a vacuum ambience. Nitrogen exposure was found to have little effect on the stress. The effect of the moisture content of air on the stress was also examined. The evolution of the stress was found to depend also on the film preparation conditions. The results strongly suggest that postplasma reactions involving active chemical species trapped in the film during deposition play an important role in the development of the stress.

I. INTRODUCTION

Adhesion to the substrate is a very critical aspect in plasma-deposited organic polymer films. Buckling and cracking are very often observed in these coatings even when the substrates are carefully cleaned prior to film deposition. The adhesion forces between a plasma polymer film and the substrate are usually small and may be overcome by the forces due to the film residual stress. Therefore, investigations of the stress dependence on the film deposition parameters and on the postdeposition environment are of capital importance when technological applications of plasma polymer films are envisaged.

Even though a large number of studies on the mechanical stress of metallic,[1] semiconducting,[2] and dielectric films[3] have been published, only a few studies on the stress of plasma polymer films have been reported. Yasuda, Hirotsu, and Olf[4–6] have studied the stress in plasma polymer films obtained from a number of monomers. They reported stress measurements as a function of film thickness and mole ratios in mixtures of comonomers. In all the films the stresses were either compressive or zero. The compressive stress was atributed to the wedging effect of attached reactive species from the plasma (ions, excited molecules, and free radicals) between existing polymer chain segments.

After deposition of a polymer film, it is to be expected that any physical or chemical process tending to change the volume of the film results in a change of its residual stress. Because one of the interfaces of the film is constrained to the substrate, compressive or tensile stresses will be developed for increasing and decreasing film volumes, respectively. Absorption of chemical species from the air or any other environment may produce expansive forces in the polymer matrix giving rise to volume expansion. Another possible source of volume change are the postplasma reactions involving reactive species in the polymer film. As shown by electron-spin-resonance (ESR) studies,[7] plasma polymers may contain a large concentration of trapped free radicals, depending on the starting monomer and on the polymerization conditions. Reactions involving these free radicals may result in modifications of the polymeric structure thus affecting the film volume.

The ESR results of Morosoff *et al.*[8] for several plasma-polymerized films have shown wide variations depending on the free-radical concentration from one polymer film to another. A comparison between plasma-polymerized acetylene (PPA) and plasma-polymerized tetramethyldisiloxane (PPTMDS) films shows that the free-radical concentration in PPA can be about 100 times higher than in PPTMDS. Yasuda and co-workers[6] reported a stress of 0.038 GPa for a PPA film while for PPTMDS no stress was detected. These results indicate that trapped free radicals play an important role on the stress of plasma-polymerized films.

In this study we investigate the evolution of the residual stress of plasma-polymerized acetylene films in vacuum and in air, oxygen, and nitrogen atmospheres. The films were prepared in direct current (dc) and radio-frequency (rf) discharges of acetylene. Because plasma-polymerized acetylene films usually contain, just after deposition, a large concentration of free radicals, they are particularly suitable for investigating possible correlations between stress and postplasma reactions.

II. EXPERIMENT

A. Film deposition

The polymer film depositions were carried out in two experimental systems using dc and rf glow discharges. In the dc system, the discharge was produced inside a stainless-steel vacuum chamber by means of two horizontal water-cooled copper electrodes, 10-cm in diameter and 5 cm apart. Substrates were placed on the grounded lower electrode or anode, while the cathode was connected to a negative dc power supply (0–4 kV). Acetylene (purity better than 99.5%) was admitted to the chamber by means of a leak valve. The gas flow was monitored by a flowmeter and the pressure in the chamber was measured by a thermocouple gauge. Prior to the deposition, the chamber was pumped down by a diffusion pump to the 10^{-4}-Pa range for about 5 min, as indicated by a Penning gauge. During the deposition, the chamber was pumped by a 12-m^3/h two-stage rotary pump.

In the the rf system, the films were obtained in a Pyrex 7-cm-diam gas-flow-type reactor. Glow discharge was sustained by means of two external ring electrodes, 7 cm apart, capacitively coupled to the rf generator (120 MHz, 80 W). A coupling circuit provided impedance matching between the discharge and the generator. The transmitted and reflected rf power were measured by a throughline wattmeter. The substrate holder was grounded. Depositions were carried out with the chamber being continuously evacuated by a 12-m^3/h two-stage rotary pump while acetylene was admitted by a leak valve. A thermocouple gauge was used for the pressure measurements. Following the same procedure for dc film deposition, the reactor was pumped down by a diffusion pump before starting the acetylene discharge.

Corning glass strips measuring $3.0 \times 0.30 \times 0.015$ cm^3 were used as substrates. Film thicknesses were determined by a Varian A-scope multiple-beam interferometer.

B. Stress measurements

Stresses of the polymer coatings were determined by the well-known equation[9]

$$\sigma = \frac{E}{6(1-v)} \frac{t^2}{t_f} \left(\frac{1}{R_f} - \frac{1}{R_i} \right), \tag{1}$$

where σ is the stress, E, v, and t are the Young's modulus, Poisson ratio, and substrate thickness, respectively, t_f is the film thickness, and R_i and R_f are the substrate radius of curvature, respectively before and after film deposition. For the glass substrates used (soda-lime), $E = 7.0 \times 10^{10}$ Pa and $v = 0.22$.

The radii of curvature of the substrates were measured by the bending beam method, using a He-Ne laser.[11] The measuring apparatus is described schematically in Fig. 1. Basically, it consists of the specimen chamber and the optical system. The chamber is provided with a fixture for holding the specimens (film-coated substrates) and can be either evacuated by a charcoal sorption pump or filled with air, oxygen, or nitrogen. In order to perform stress measurements in air of low water vapor content, a moisture
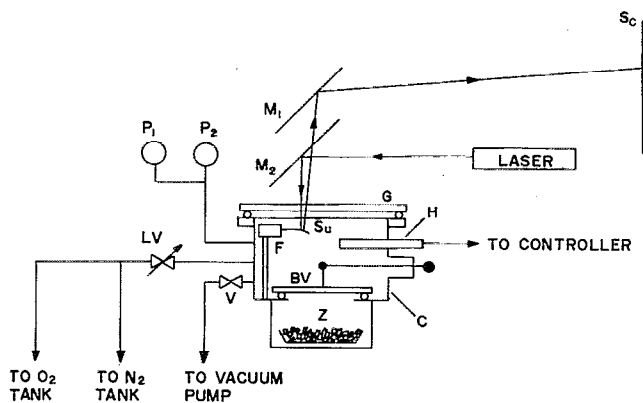

FIG. 1. Schematic diagram of the stress-measuring apparatus. C: chamber; Su: specimen (film-coated substrate); F: fixture for holding the film; G: glass plate; BV: baffle valve; Z: zeolite moisture trap; H: hygrometer; LV: leak valve; V: high-vacuum valve; P_1: Pirani pressure gauge; P_2: diaphragm pressure gauge; M_1: mirror; M_2: semitransparent mirror; Sc: screen board.

trap consisting of a dish of artificial zeolite pellets (Linde, 5 Å) was installed in the lower compartment of the chamber. Since zeolite has no pumping action on oxygen and nitrogen at room temperature, only water vapor was trapped when the baffle valve of the chamber was opened. The relative humidity in the chamber was measured by an electronic hygrometer (Vaissala model HMI 31)

The optical system is comprised by a low-power laser, two parallel mirrors, and a vertical screen board covered with paper for recording the laser spots reflected from the film. By means of a micrometer screw, the parallel mirrors were horizontally translated, thus changing the point of incidence of the laser beam on the film. For the determination of the radius of curvature R of the substrate, the following formula was used:

$$l = (R/2L)x, \tag{2}$$

where l is the distance between the fixture edge and the laser beam spot on the sample, L is the optical path length from the substrate to the screen, and x is the vertical distance on the screen from the laser spot to an arbitrary point 0. From the slope of the straight-line plot of l vs x, the value of R was calculated. Each sample was measured in ten positions, by sweeping the film lengthwise with the laser beam. Equation (2) holds only when $R \gg l$. In our experiments, R was in the range from 300 to 1500 cm and l was at most 2.5 cm. The value of L was 312 cm.

The relatively poor definition of the laser spot in the screen, due to the low reflectivity of the polymer films, was the main source of errors in the determination of the stress. This led to a considerable scattering of data points in the plots of the stress as a function of time. For some films studied, the uncertainty in the determination of the radius of curvature R was found to be as high as 10%.

III. RESULTS AND DISCUSSION

The evolution of the residual stress with time for various plasma-polymerized acetylene films in vacuum, air,

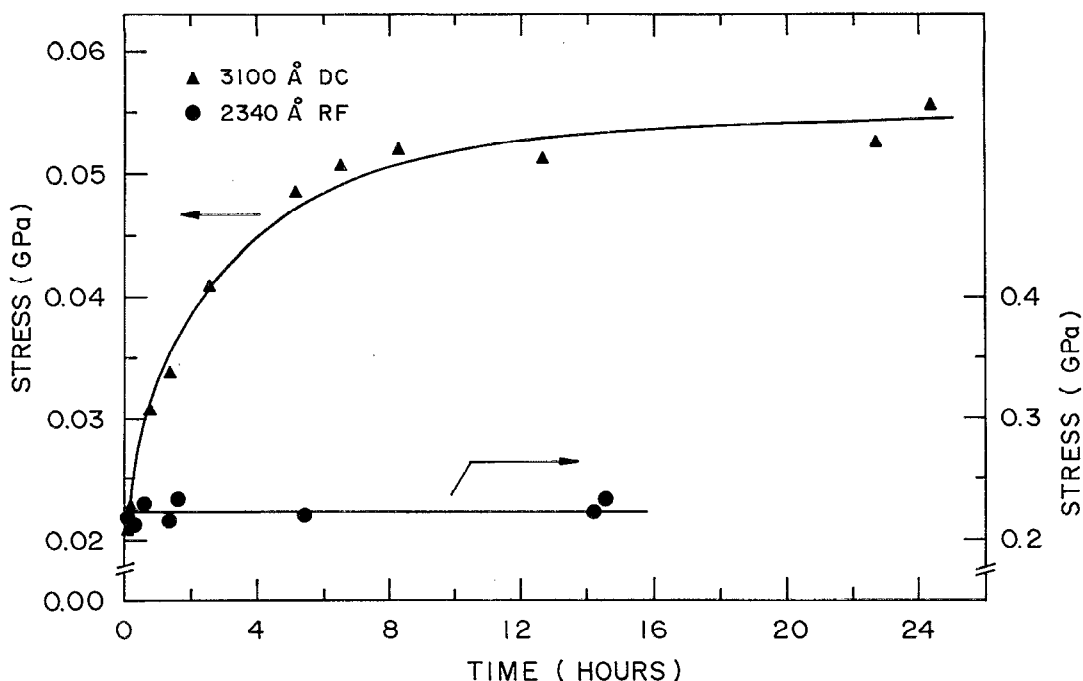Shiosawa, Moraes, and Scarminio   4884

FIG. 2. Dependence of the residual stress on time for films in vacuum. Films prepared in dc and rf discharges. Deposition parameters: cathode voltage $V_c = -3000$ V and acetylene pressure $P_A = 9.3$ Pa (dc film); rf power $P_{rf} = 17$ W and $P_A = 9.3$ Pa (rf film). Note that the left-hand-side scale applies to the upper graph and the right-hand-side scale to the lower graph.

oxygen, and nitrogen are shown in Figs. 2–7. Except where it is specifically stated, the origin of the time scale of the plots corresponds to the time at which the film deposition was finished. Compressive stresses were observed in all films studied. The initially measured values of the stresses were in the range from 0.015 to 0.25 GPa.

A. Stress measurements in vacuum

Figure 2 shows plots of the residual stress as a function of time for films prepared in dc and rf discharges. Measurements were made with the specimens in vacuum ($\cong$ 0.1 Pa).

For the rf-prepared film, except for some fluctuations in the data points due to experimental errors, the stress remains constant for over 14 h in vacuum. An entirely different time dependence is observed for the dc-prepared film. The stress increases sharply from $\cong 0.021$ to 0.042 GPa in the first 3 h in vacuum, reaching a value of $\cong 0.054$ GPa after 24 h. This behavior can be readily interpreted as a consequence of time-dependent modifications in the polymeric structure due to reactions between active chemical species trapped in the film during deposition. It is very likely that these reactions produce changes in bond lengths, thus leading to an overall modification of the polymer volume. Reactions of this kind are well known to occur.[12] Since there is an increase in the compressive stress with time in the dc film of Fig. 2 it seems that reactions giving rise to volume increase predominate.

Because the thicknesses of the films of Fig. 2 are not too far apart (2340 and 3100 Å), the widely different dependencies of the stresses with time can be readily interpreted as a consequence of the differences between the two deposition procedures (dc and rf). In fact, the free-radical concentration of plasma-polymerized acetylene is found to depend strongly on the discharge conditions.[8,13]

B. Stress measurements in air

For all films exposed to ambient air it has been found that the stress increased monotonically with time. The behavior of the stress with time, however, varied strongly from one film to another. This is illustrated in Fig. 3, which shows stress versus time curves for two films obtained in the dc system in different conditions. In the first 30 h of air exposure, a change in the stress of one order of magnitude is observed for the film of 3140 Å while for the film of 9820 Å the stress changes by a factor of 1.6. In none of the films obtained was a constant value of the stress reached during the time of exposure to air. For the film of 3140 Å, for example, the stress keeps rising even after 48 h in air. The monotonically decreasing rate of stress change with time for the films of Fig. 3 is typical of all the films exposed to air.

In order to compare the behavior of the stress with time for all the films exposed to air, we have arbitrarily defined for each film the ratios

$$a_5 = \sigma_5/\sigma_0 \quad \text{and} \quad a_{30} = \sigma_{30}/\sigma_0,$$

where σ_0, σ_5, and σ_{30} are the stresses at 0, 5, and 30 h, respectively. The value of σ_0, or the initial stress, was obtained by extrapolation of the stress vs time data to $t = 0$. The short-term stress evolution is indicated by the value of a_5, while the value of a_{30} indicates the long-term stress evolution. For some of the films, 30 h was the maximum exposure time.

Table I lists the value of σ_0, a_5, and a_{30} for several films obtained in the dc and rf systems and exposed to air. The wide range of variation of parameters a_5 and a_{30} for samples 1–4, obtained with the same plasma conditions (acetylene pressure and cathode voltage), shows that the evolution of the stress depends strongly on the film thickness. For these samples, at any given time $t < 30$ h, the rate of
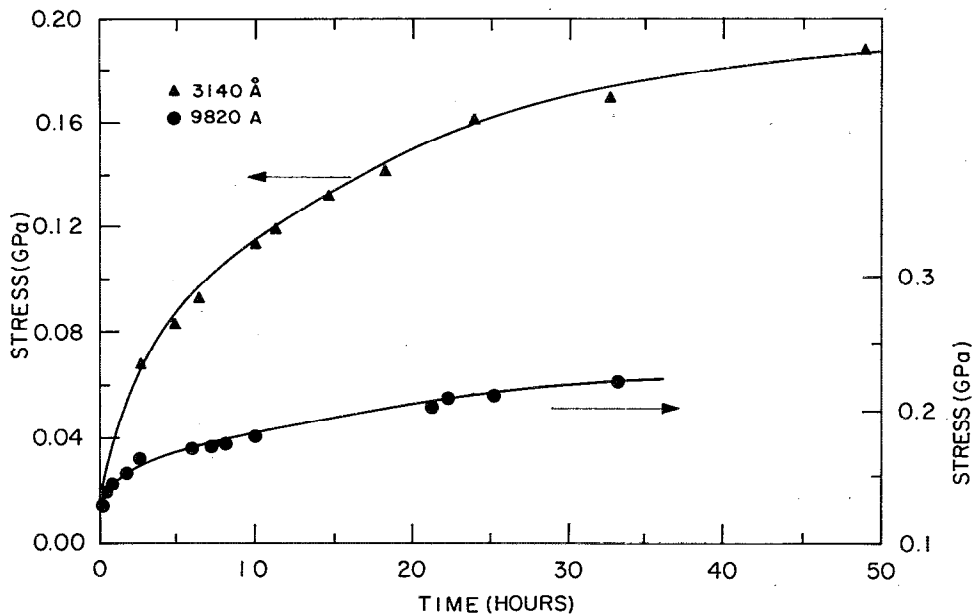
FIG. 3. Residual stress as a function of time for films prepared in the dc system and exposed to ambient air. Deposition parameters: $P_A = 9.3$ Pa for both films; ●: $V_c = -2000$ V; ▲: $V_c = -3000$ V. Note stress scales.

the stress variation $d\sigma/dt$ increases with decreasing film thickness. A comparison between samples 3 and 6, whose thicknesses are similar, illustrates the strong dependence of the evolution of the stress on the film deposition parameters. We also found that the evolution of the stress depends on the rf power applied to the acetylene plasma (samples 7 and 8).

For the development of the stress in air, we have to consider: (i) the effect of absorbed chemical species from the air, which may or may not react with other species in the film; and (ii) the effect of reactions between trapped active species originating from the plasma. As previously discussed, effect (ii) may be responsible for stress increments in vacuum. From a comparison between the stress evolution curves for the film of 3100 Å in vacuum (Fig. 2) and for the film of 3140 Å exposed to air (Fig. 3) it can be appreciated that at any time t, the rate of increase in stress with time is greater in the film exposed to air. Since both films have nearly the same thickness and were obtained under the same conditions, we conclude that the absorp-

tion of chemical species from air is the major contribution to the increase in the stress.

Since our results show that exposure to air affects the residual stress of plasma-polymerized acetylene films, it remains to investigate which one of the air components (water vapor, oxygen, or nitrogen) is most likely responsible for the stress increments.

C. Influence of water vapor on the stress

Investigations of the role of water vapor on the stress of our plasma-polymerized films were carried out in two samples prepared in dc and rf discharges. Each sample was mounted in the stress measuring chamber and initially exposed to ambient air of 65% relative humidity for over 20 h. During this time, stress increments from 0.18 to 0.46 GPa and from 0.20 to 0.29 GPa were then measured for the dc and rf films, respectively. The chamber was then closed with a glass plate cover, the baffle valve of the apparatus was opened, and the removal of water vapor from the enclosed air by the zeolite pellets was initiated. The relative humidity content in the chamber changed from 65% to a minimum of 12% in about 30 min in each experiment. Figure 4 shows the behavior of the stress with time for each film upon moisture removal. Both plots exhibit sharp stress decays showing that water vapor does play a role on the stress. As can be observed in the plots, the decrease in the relative humidity from 65% to 12% produced stress decrements of 0.04 and 0.02 GPa in the dc and rf films, respectively.

Absorption of water by polymers is a commonly observed phenomenon.[14] In our plasma polymer films we assume that absorbed water molecules may contribute to the stress (i) by the wedging effect of unreacted water molecules between the polymer chains, or (ii) by structural changes induced by chemical reactions between water and reactive species trapped in the polymer film.

TABLE I. Initial stresses and stress ratios for films prepared in dc and rf discharges and exposed to ambient air. V_c: cathode voltage; P_{rf}: rf power; t_f: film thickness; σ_0: initial stress; a_5: ratio of the stress at 5 h to the initial stress; a_{30}: ratio of the stress at 30 h to the initial stress. All films were deposited with an acetylene pressure of 9.3 Pa.

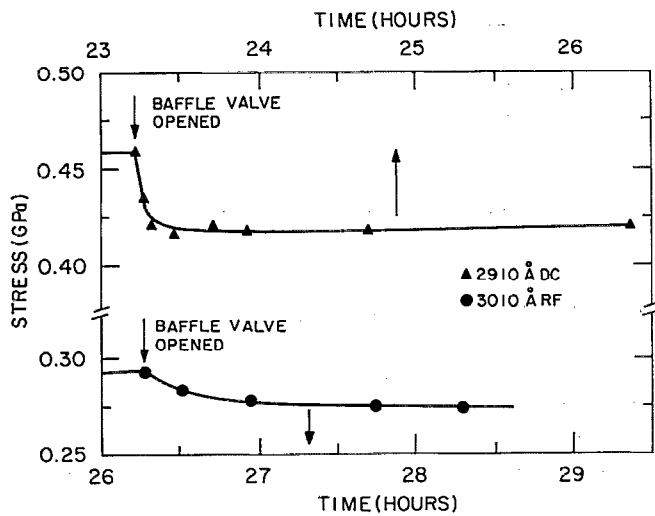| Sample	V_c (V)	P_{rf} (W)	t_f (Å)	σ_0 (GPa)	a_5	a_{30}
1	− 2000	···	2160	0.20	1.8	2.4
2	− 2000	···	3990	0.18	1.7	2.3
3	− 2000	···	8810	0.16	1.4	1.8
4	− 2000	···	9820	0.13	1.3	1.6
5	− 3000	···	3140	0.017	5.0	10
6	− 3000	···	8960	0.015	4.9	8.5
7	···	17	3470	0.23	1.2	1.3
8	···	24	3600	0.21	1.3	1.6

FIG. 4. Stress decrements with time due to the decrease of moisture content of air. Films obtained in dc and rf discharges. Relative humidity change from 65% to 12% for both films. Deposition parameters: $V_c = -2000$ V and $P_A = 9.3$ Pa (dc film); $P_{rf} = 17$ W and $P_A = 9.3$ Pa (rf film). Note that the upper time scale applies to the upper graph and the lower to the lower graph.

The stress decrements in Fig. 4 are readily interpreted as a consequence of water molecules diffusing out of the polymer samples. The very pronounced differences between the rate of the stress decay of these films reflects the distinctions in their polymeric structures. It is very likely that these decrements are due only to unreacted water molecules. It is possible however that a portion of the water molecules remained irreversibly absorbed as a consequence of reactions with active chemical species in the bulk of the films.
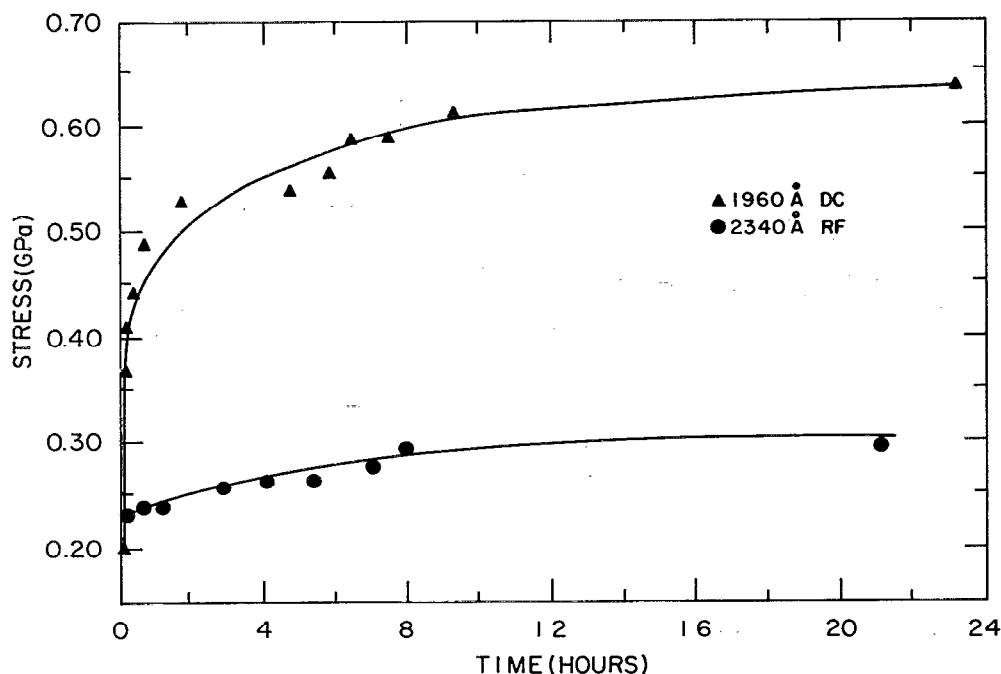
D. Stress measurements in oxygen and in nitrogen

For the stress measurements in oxygen and nitrogen atmospheres, as soon as the samples were mounted in the measuring apparatus, the chamber was evacuated to $\cong 0.1$ Pa. The valve of the vacuum pump was then closed, and oxygen or nitrogen was admitted to the chamber by the leak valve, up to a pressure of 10^5 Pa.

The evolutions of the stress for dc and rf films under oxygen at 10^5 Pa are plotted in Fig. 5 as a function of time. The widely different behavior of the stress between the two films is once more interpreted as a consequence of differences in the structure and properties between dc and rf films. Oxygen deeply affects the stress of the dc film: An increment from 0.20 to 0.61 GPa is observed in the first 10 h of exposure. However, most of the stress increase develops in less than 1 h in oxygen. The small effect of oxygen on the rf film is reflected in the small rise in the stress, from 0.23 to 0.30 GPa, during over 20 h of oxygen exposure.

Subsequent to the oxygen exposure, a vacuum of $\cong 0.1$ Pa was produced in the stress measuring chamber. The behavior of the stress with time for each of the films is presented in Fig. 6, showing that oxygen begins to desorb from the films as soon as pumpdown is initiated. For the rf film, after about 1 h of pumping, the stress returns to nearly the same value as in the beginning of the oxygen exposure. This result suggests that the increase in the stress for the rf film arises from unreacted absorbed oxygen molecules. On the other hand, for the dc film, the stress decrement is very small if compared to the large increment due to oxygen exposure. This clearly indicates that only a fraction of the initially absorbed oxygen has diffused out of the film when the chamber is evacuated; the other fraction probably underwent chemical reactions in the bulk of the film, thus remaining irreversibly absorbed. In fact, from

FIG. 5. Plots of the residual stress vs time for films obtained in dc and rf discharges and exposed to oxygen at 10^5 Pa. Deposition parameters: $V_c = -2000$ V and $P_A = 9.3$ Pa (dc film); $P_{rf} = 17$ W and $P_A = 9.3$ Pa (rf film).
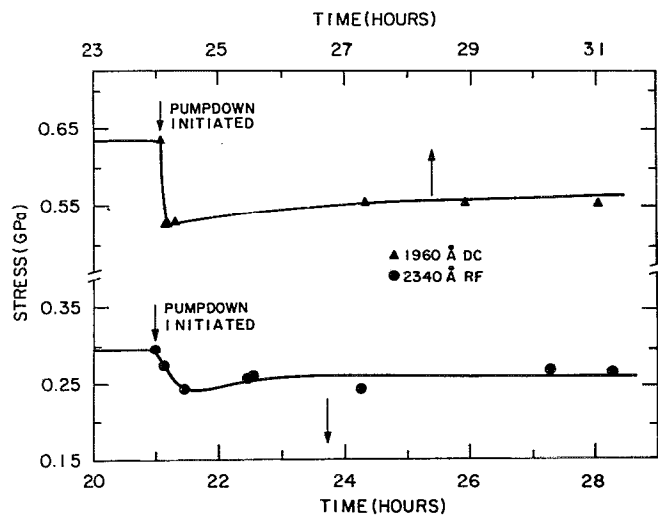
FIG. 6. Stress decrements with time due to the decrease of the oxygen pressure in the chamber. Films obtained in dc and rf discharges. Deposition parameters: $V_c = -2000$ V and $P_A = 9.3$ Pa (dc film); $P_{rf} = 17$ W and $P_A = 9.3$ Pa (rf film). Note time scales.

elemental analysis of plasma-polymerized acetylene films, some investigators[15] have observed a fairly large oxygen content, considered to be a consequence of the postplasma reactions of trapped radicals with oxygen from the ambient air. Furthermore, oxygen is known to react with many kinds of organic polymers producing chain degradation[16] and affecting its chemical and physical properties. Thus, the large increase in the stress for the dc film of Fig. 5 is very likely related to structural modifications in the polymeric chains, induced by chemical reactions with oxygen, leading to volume expansion.

The effect of nitrogen at 10^5 Pa on stress was studied in two films obtained in dc and rf discharges. Figure 7 shows the dependence of the stress on time for dc and rf films in nitrogen and for a dc film in a vacuum of $\cong 0.1$ Pa. The dc films have nearly the same thickness and were prepared under identical conditions.

For the rf film, no increase in the stress was detected. From a comparison between the plots for the dc films in vacuum and under nitrogen it can be concluded that nitrogen has only a small effect on the stress. The development of the stress in both dc films seems to be almost entirely due to the structural changes arising from reactions between active species trapped in the film during deposition.

IV. CONCLUSIONS

We have studied the evolution of the residual stress in plasma-polymerized acetylene films as a function of time in vacuum and in air, oxygen, and nitrogen atmospheres. Increasing compressive stresses were observed in most of the films. As a general trend, for a given time interval and environment in the stress measuring chamber, the stress increments in the dc films were larger than in the rf films. This difference was attributed to distinctions in structural and chemical properties between the two kinds of film.

Very large time-dependent increments of the stress were observed in some of the films in vacuum and in air and oxygen atmospheres. For the films in vacuum, the stress increments were interpreted as a consequence of increases in the film volume due to postplasma reactions between active species originating from the plasma and
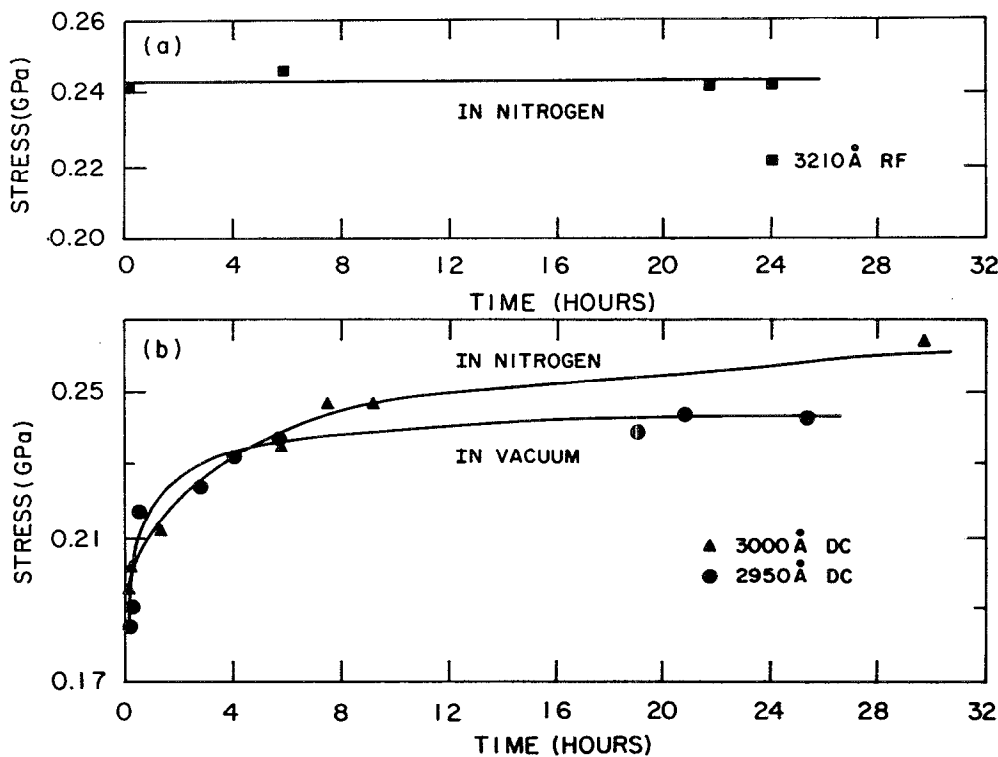

FIG. 7. Residual stress as a function of time for films obtained in dc and rf discharges. (a) rf film exposed to nitrogen at 10^5 Pa. (b) dc films in nitrogen at 10^5 Pa and in vacuum at 0.1 Pa. Deposition parameters: $V_c = -2000$ V and $P_A = 9.3$ Pa (dc films); $P_{rf} = 12$ W and $P_A = 9.3$ Pa (rf film).

trapped in the film during deposition. For the films in air and in oxygen, reactions between oxygen and these active species can be interpreted as the main cause of the volume changes. Our results indicated that absorbed unreacted oxygen and water molecules contribute, even more weakly, to the increase in the stress. The contribution of nitrogen to the stress was found to be very small for a dc film and negligible for a rf film.

ACKNOWLEDGMENTS

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