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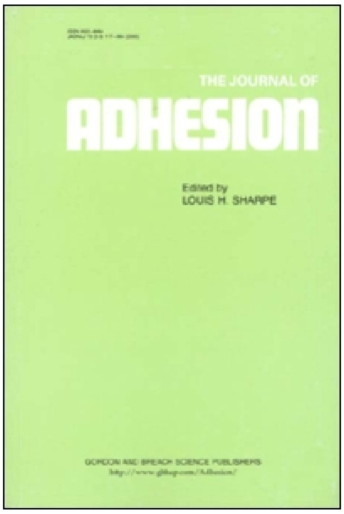

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Surface and Corrosion Characteristics of a-C:H/Fluorocarbon Films*

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Fluorocarbon films were deposited on type 301 stainless steel substrates from mixtures of hexafluoroethane (HFE) or hexafluoroacetone (HFA) and acetylene and argon in a radio-frequency (13.56 MHz) plasma discharge. A 10 nm thick polysilicon interlayer was deposited prior to fluorocarbon film deposition to obtain good adhesion. To prevent film failure, a-C:H layer was deposited on the polysilicon layer prior to fluorocarbon film deposition, resulting in a-C:H/fluorocarbon composite film structures. The influence of the feed gas composition on the properties of the layered structure was investigated. Surface energies of the films were calculated from the film contact angle values obtained with water and diiodomethane. The composition of the surface layer of these films was characterized using X-ray photoelectron spectroscopy (XPS). The resistance offered by these a-C:H/fluorocarbon film structures to anodic breakdown in an electrolyte containing 0.1 M NaCl and 0.1 M Na_2SO_4 was studied using a potentiostatic technique. The anodic current density for the coated type 301 stainless steel samples was at least 3 orders of magnitude smaller than that for the bare sample and more than an order of magnitude smaller than that observed with samples coated with only the (equally thick) a-C:H layer. The resistance offered by the layered coatings to solution penetration increased with increasing fluorine content in the films.

Keywords: Low surface energy; fluorocarbon films; amorphous carbon films; corrosion characteristics; plasma deposition; anodic breakdown

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INTRODUCTION

Fluorinated coatings, such as coatings comprised primarily of poly-(tetrafluoroethylene) (PTFE) or other highly fluorinated polymers, are often used in applications which require low surface energies. However, fluorinated coatings deposited by conventional coating technologies have a number of problems. Adhesion of the coating to the substrate is often poor. The presence of solvent in the coating formulation can lead to environmental problems that limit their usefulness. Plasma-polymerized fluorocarbon (PPFC) films overcome many of these problems [1]. They are prepared from a gas-phase fragmentation of monomers in a low-pressure plasma discharge into a variety of reactive ions, radicals, and excited molecules, the types and distribution of which are determined by the gases fed into the system and by the process conditions [2, 3]. Interaction of these species with each other and with the substrate determines the final composition and structure of the film.

Reaction of fluorocarbons in a plasma reactor represents a balance between etching by highly reactive fluorine atoms and polymerization [2, 4, 5]. In the case of cyclic or unsaturated monomers such as hexafluoroacetone (HFA), deposition is favored over etching, resulting in polymer films; whereas, with saturated monomers such as hexafluoroethane (HFE), etching is favored over deposition. So, saturated monomers were rarely used for plasma polymerization. However, it was demonstrated that PPFCs can be produced using saturated monomers, such as HFE, if the substrate is capable of participating in the deposition process [6, 7]. It has been shown here that HFE can be used for plasma deposition of fluorocarbon films on non-reactive substrates, if used in combination with a hydrocarbon co-reactant.

In this study, the surface energies of a series of PPFC films deposited from HFE/acetylene and HFA/acetylene mixtures on stainless steel substrates are analyzed in order to investigate the role of feed gas mixture on film composition and properties. Although HFA has been used as a feed gas in previous investigations [7, 8, 9], a full study of the influence of fluorocarbon/hydrocarbon ratio and of hydrocarbon type on film surface energy has not appeared.

Since fluorocarbon films are known to pose problems of adhesion to their substrates [10], a hydrogenated amorphous carbon (a-C:H) layer was deposited on the stainless steel substrate prior to fluorocarbon film deposition. But, when the substrate is a metal, as is the case here, even the hydrocarbon films displayed poor adhesion and/or film lift-off. Hence, a 3-layered structure, consisting of a thin polysilicon adhesion-promoting layer [11], followed by a hydrogenated amorphous carbon (a-C:H) layer, and a final fluorocarbon layer, was deposited on stainless steel substrates and investigated in this study. The fluorocarbon films, prepared from feed gas mixtures containing 0–100% hydrocarbon co-reactant, were deposited atop the a-C:H layer and characterized by contact angle measurements and X-ray photoelectron spectroscopy (XPS). The influence of feed gas composition on the surface energies of the deposited films was explored.

An important characteristic of fluorocarbon films is chemical inertness even in very reactive environments. Hence, their ability to offer protection from corrosion to the underlying metallic substrate is of interest. In this paper, the corrosion characteristics of some of these films have also been studied using the standard potentiostatic technique [12].

EXPERIMENTAL

A commercial parallel-plate plasma reactor (PlasmaTherm model 730), was used for deposition of all films. The chamber consists of two parallel electrodes, the upper one being grounded and the lower one powered. The chamber walls are grounded. Removal of heat from the electrodes is accomplished *via* a fluid jacket in which cold water is circulated. Four outlet ports, at the four corners of the lower wall of the reactor, lead the gases to a Roots blower backed by a mechanical pump. The base pressure in the reactor is lower than 1 mTorr. A 750-W generator delivers radio-frequency (RF) power at 13.56 MHz through an automatic matching network to the reactor. The reflected power is typically less than 4 watts. The feed gases flow radially outward from the perforated upper electrode in a shower-head configuration. All the films were deposited on 76.2 μm thick type 301 stainless steel substrates, placed on the lower powered electrode.

Prior to film deposition, the stainless steel substrate was cleaned for 1 min in a pure argon plasma at a flow rate, pressure and RF power of

50 sccm, 25 mTorr, and 150 W, respectively. A polysilicon layer, approximately 10 nm thick, was deposited on the cleaned substrate from a plasma created from 2% silane in argon at a total flow rate of 50 sccm, a pressure of 25 mTorr, and an RF power of 150 W. The deposition time was 4 min.

The a-C:H and fluorocarbon layers were deposited using the conditions listed in Tables I and II. Samples were labeled according to the

TABLE I Conditions for the deposition of films from acetylene/hexafluoroethane mixtures

Sample	*Step*	*HFE Reactant Gas (%)*	*Gas Flow Rate (sccm)*			*RF Power (W)*	*Pressure (mTorr)*	*Negative Bias Voltage (V)*	*Duration (min)*
			C_2H_2	*Ar*	*HFE*				
Ac/HFE-100	1	0	3.2	12.8	0	100	50	220	2
	2	67	3.2	12.8	6.4	100	100	135	1
	3	80	3.2	12.8	12.8	100	100	158	1
	4	86	3.2	12.8	19.2	100	100	158	1
	5	90	3.2	12.8	28.8	100	100	120	3
	6	100	0	0	28.8	100	100	70	2
Ac/HFE-90	1	0	3.2	12.8	0	100	50	225	2
	2	90	3.2	12.8	28.8	100	100	95	8
Ac/HFE-70	1	0	9.6	38.4	0	100	50	230	2
	2	70	9.6	38.4	22.4	100	100	128	8
Ac/HFE-50	1	0	16	64	0	100	50	230	2
	2	50	16	64	16	100	100	128	4
Ac/HFE-25	1	0	24	96	0	100	50	216	2
	2	25	24	96	8	100	100	127	4
Ac/HFE-0	1	0	32	116	0	100	100	155	6

TABLE II Conditions for the deposition of films from acetylene and hexafluoroacetone

Sample	*Step*	*HFA reactant gas (%)*	*Gas Flow Rate (sccm)*			*RF Power (W)*	*Pressure (mTorr)*	*Negative Bias Voltage (V)*	*Deposition time (min)*
			C_2H_2	*Ar*	*HFA*				
Ac/HFA-0	1	0	32	116	0	100	100	155	6
Ac/HFA-50	1	0	14	56	0	100	50	235	2
	2	50	14	56	14	100	100	137	4
Ac/HFA-70	1	0	8.4	33.6	0	100	50	220	2
	2	70	8.4	33.6	19.6	100	100	103	8
Ac/HFA-90	1	0	2.8	11.2	0	100	50	220	2
	2	90	2.8	11.2	25.2	100	100	70	8

reactant feed gases used to produce the outermost layer. Samples prepared from acetylene (Ac) and hexafluoroacetone (HFA) feed gases were labeled Ac/HFA-xx, while samples prepared from acetylene (Ac) and hexafluoroethane (HFE) feed gases were labeled Ac/HFE-xx, where xx indicates the percentage of the fluorocarbon monomer in the feed gas mixture. Argon was always present in the feed gas mixture at a flow rate that was four times that of the hydrocarbon but was not used in the calculation of the percentage of fluorocarbon monomer. Presence of argon in the feed gas stream increases the hardness, and therefore the protection ability, of the films [13, 14].

Surface Energy Measurement

The film surface energy was calculated using the equation given by Owens and Wendt [15] as follows.

$$1 + \cos\theta = 2\sqrt{\gamma_s^d}\left(\frac{\sqrt{\gamma_l^d}}{\gamma_l}\right) + 2\sqrt{\gamma_s^p}\left(\frac{\sqrt{\gamma_l^p}}{\gamma_l}\right)$$

where,

γ_l = surface energy of the liquid
γ_s = surface energy of the solid
Θ = contact angle of the solid with the liquid
$\gamma = \gamma^d + \gamma^p$

The superscripts *d* and *p* denote the dispersive and the polar components of surface energy, respectively. The contact angle values of the film with water and diiodomethane, measured using 5 μL drops in a stationary mode, along with the known values of γ^d and γ^p for these liquids, were substituted in the above equation and the resulting simultaneous equations were solved to obtain the dispersive and the polar components of the surface energy of the film. Owens and Wendt [15] observed a good correlation between surface energies calculated by this method and those determined using the method suggested by Zisman [16]. So, the surface energies reported here are assumed to be reasonable approximations of values obtained by other methods. The contact angle data on the films discussed here are given in Table III.

X-Ray Photoelectron Spectroscopy

The X-ray photoelectron spectroscopy (XPS) measurements were made at Eastman Kodak Company using a Physical Electronics 5601 photoelectron spectrometer with monochromatic Al Kα X-rays (1486.6 eV). The X-ray source was operated with a 7 mm filament at 200 W. Charge neutralization for these insulating materials was accomplished by flooding the sample surface with low energy electrons ($\leqslant 25$ mA emission current, $\leqslant 0.5$ eV bias voltage) from an electron gun mounted nearly perpendicular to the sample surface. The pressure in the spectrometer during analysis was typically below 6.5×10^{-8} Pa. For the high-resolution spectra, the analyzer operated at a pass energy of 11.75 eV. All spectra were referenced to the C 1s peak for neutral (aliphatic) carbon atoms, which was assigned a value of 284.6 eV. Peak-fitting to determine CF, CF_2 and CF_3 contents was done using a least-squares deconvolution routine employing line shapes with 90% Gaussian/10% Lorentzian character. Spectra were taken at a 45° electron takeoff angle, which corresponds to an analysis depth of ~ 5 nm. Errors in compositions reported by XPS are estimated to be ± 2–3%.

TABLE III Film contact angle values with water and diiodomethane

Sample	*Contact angle (degrees)*	
	water	*diiodomethane*
Ac/HFE-100	98	78
Ac/HFE-90	101	72
Ac/HFE-70	83	46
Ac/HFE-50	76	40
Ac/HFE-25	75	28
Ac/HFE-0	63	18
Ac/HFA-90	98	76
Ac/HFA-70	98	68
Ac/HFA-50	77	41
Ac/HFA-0	63	18

RESULTS AND DISCUSSION

Films Deposited from HFE

The surface energies of the films, shown in Figure 1, varied from a high value of 52 mN/m for the film prepared from the pure acetylene reactant gas (Ac/HFE-0) to 20 mN/m for the film prepared from the pure HFE reactant gas (Ac/HFE-100). The value for Ac/HFE-100 closely matches that determined for a film deposited from HFE reactant gas in an RF glow discharge reactor onto a polyethylene substrate, measured at 21 mN/m [7]. A gradual decrease in surface energy is seen as the HFE feed gas concentration is increased from zero to 70%; however, a significant drop in surface energy is seen as the HFE concentration is increased further from 70% to 90%.

X-ray photoelectron spectroscopy (XPS) was used to characterize the surface composition of the films. The spectra were deconvoluted

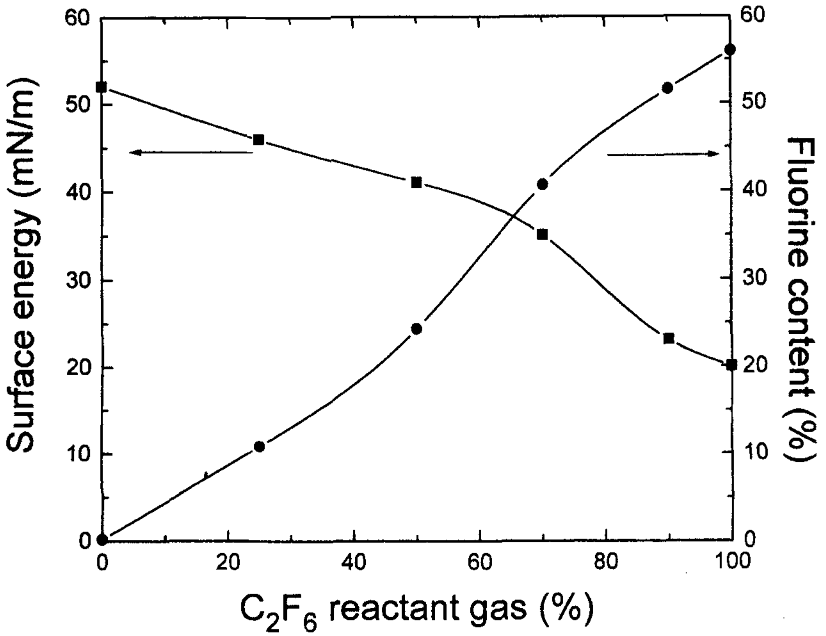

FIGURE 1 Variation in surface energy and surface fluorine content as a function of HFE content in acetylene/HFE mixtures.

into five peaks, assigned in order of decreasing binding energy to CF_3, CF_2, CF, $\underline{C}$—CF_n, and $\underline{C}$—C_n, as described elsewhere [17]. The relative concentrations of the three fluorocarbon species are listed in Table IV. The film formed from the pure HFE reactant gas shows a high concentration of fluorine on the film surface. As the concentration of HFE reactant gas decreases, however, the fluorocarbon distribution shifts to favor the less highly fluorinated species. The exception is the Ac/HFE-90 sample, in which the CF_3 concentration has increased while the CF_2 and CF concentrations remain unchanged.

The elemental composition of the film surfaces was determined by peak fitting of XPS survey spectra. Integration of the area under the curves was followed by multiplication by the appropriate sensitivity factor for each element to provide the elemental compositions reported in Table IV. The variation of fluorine content with reactant gas composition is also shown in Figure 1. A nearly-linear increase in fluorine content with increasing HFE reactant gas is observed. The large change in the slope of the surface energy *vs.* HFE concentration curve is not mirrored in the fluorine content curve, providing further evidence that surface energy is determined not by the fluorine content of the film alone but also by the distribution of fluorine atoms in the fluorocarbon species. As expected, the carbon concentration in the films increases as the HFE reactant gas concentration decreases.

Films Formed from HFA

Contact angle data were again used to calculate the surface energies of films prepared from Ac/HFA feed gas mixtures containing 0–90%

TABLE IV XPS results for samples prepared from acetylene/hexafluoroethane feed gas mixtures

Sample	*Carbon (%)*	*Fluorine (%)*	*Oxygen (%)*	*Other (%)*	*Carbon Distribution*		
					CF (%)	*CF_2 (%)*	*CF_3 (%)*
Ac/HFE-100	41.9	56.0	1.6	0.5	14.7	17.1	16.6
Ac/HFE-90	45.4	51.6	2.4	0.5	14.5	17.3	20.6
Ac/HFE-70	53.1	40.7	5.5	0.7	17.5	16.9	10.5
Ac/HFE-50	68.2	24.3	7.2	0.4	19.0	11.4	7.0
Ac/HFE-25	81.9	10.8	6.7	0.5	16.3	5.0	2.1
Ac/HFE-0	90.0	0.2	9.6	0.3	–	–	–

HFA. The change in surface energy with HFA content in the Ac/HFA reactant gas mixture is shown in Figure 2. The surface energies of the films vary from a high of 53 mN/m for the film prepared from pure acetylene (Ac/HFA-0) to 21 mN/m for the film prepared from 90% HFA reactant gas (Ac/HFA-90). While some decrease in surface energy occurs when the reactant gas mixture is changed from 100% acetylene (Ac/HFA-0) to 50% HFA (Ac/HFA-50), the greatest drop in surface energy is seen when the feed gas composition is changed from 50% (Ac/HFA-50) to 70% HFA (Ac/HFA-70). The surface energy drops from 41 mN/m for Ac/HFA-50 to 25 mN/m for Ac/HFA-70. Little further change in surface energy is measured when the HFA content in the reactant gas mixture is increased to 90% (Ac/HFA-90).

The compositions of the film surfaces were characterized using X-ray photoelectron spectroscopy (XPS). The spectra for Ac/HFA-90 and Ac/HFA-70 were deconvoluted into five peaks, assigned in order of decreasing binding energy to (1) CF_3, (2) CF_2, (3) CF/C=O/C(O)F,

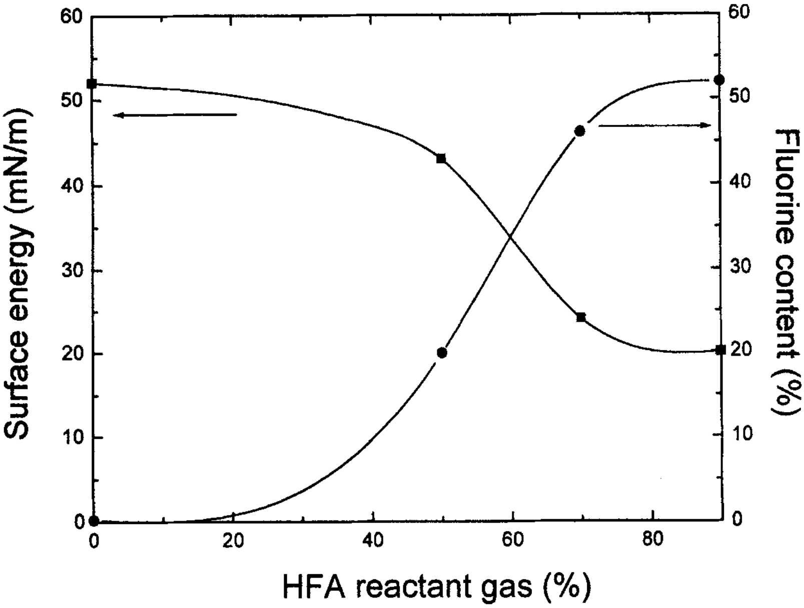

FIGURE 2 Variation in surface energy and surface fluorine content as a function of HFA content in acetylene/HFA mixtures.

(4) C—CF$_n$/C—OH, and (5) C—C$_n$, as described elsewhere [9,17,18]. An additional peak was included in the peak fitting for Ac/HFA-50 to account for further contributions due to carbon-oxygen bonding. The relative concentrations of the three fluorocarbon species in each film are listed in Table V. The presence of carbon-oxygen species in the films makes the assignment of the concentration of CF species in the films somewhat uncertain, but the CF_2 and CF_3 peaks are free from interference with overlapping oxygen peaks and allow unambiguous interpretation of their relative concentrations. The CF_3 content of the films increases with increasing HFA in the feed gas. Ac/HFA-90 has the highest CF_3 content at 22.2%, but its CF_3 content is closely matched by that of Ac/HFA-70. The data show a correlation between the CF_3 content of the films and their surface energies, with the films prepared from high HFA-content feed gases having comparable CF_3-contents and surface energies and with a sharp decrease in CF_3-content and an increase in surface energy when HFA reactant gas concentration is dropped to 50% or below. As discussed above, this demonstrates the influence of specific fluorinated species on the surface energy of the films.

The elemental compositions of the film surfaces, determined by peak fitting of XPS survey spectra, integration of the area under the curves, and multiplication by the appropriate sensitivity factors, are reported in Table V. The data show an increase in fluorine content and a decrease in carbon content with increasing HFA in the feed gas, which is indirectly related to the fluorine and carbon contents of the feed gas mixtures used to produce the films.

Oxygen is detected at low levels in all the samples. Higher levels of oxygen incorporation are observed for the films prepared from 50%

TABLE V XPS results for samples prepared from acetylene/hexafluoroacetone feed gases

Sample	*Carbon (%)*	*Fluorine (%)*	*Oxygen (%)*	*Other (%)*	*Carbon Distribution*	
					CF_2 (%)	*CF_3 (%)*
Ac/HFA-0	90.0	0.2	9.6	0.3	–	–
Ac/HFA-50	68.4	19.9	10.8	0.8	10.9	6.1
Ac/HFA-70	48.9	46.1	4.6	0.5	14.8	20.7
Ac/HFA-90	44.1	52.0	3.0	0.9	17.8	22.2

or less HFA. Higher levels of ion bombardment, resulting from the process conditions used to produce these films, probably results in the presence of a higher concentration of long-lived reactive species on the surface that can react with atmospheric oxygen. The increasing oxygen content in films prepared from decreasing HFA concentrations may explain some of the increase in surface energy observed above.

Corrosion Characteristics of a-C:H/Fluorocarbon Films

Diamond-like carbon films were previously studied for their corrosion resistance on aluminum [19] and type 301 stainless steel surfaces [20], using a potentiostatic technique [12]. They were found to reduce the corrosion rate of both Al and stainless steel substrates by about 3 orders of magnitude. It has been shown here that the inclusion of fluorine in the carbon films enhances the corrosion protection offered by these films.

The a-C:H/fluorocarbon films deposited on type 301 stainless steel substrates from HFE/acetylene mixtures were investigated for their resistance to anodic breakdown in aqueous electrolytes, again using the potentiostatic technique [12]. A variety of feed gas compositions ranging from 100% acetylene to 10% acetylene were explored to determine the role of fluorine content in influencing the resistance offered by the a-C:H/fluorocarbon film structures to solution penetration. The potentiostatic measurements on all the samples were performed at 1.5 V (SCE) in an electrolyte consisting of 0.1 M NaCl and 0.1 M Na_2SO_4 in deionized water and the resulting anodic current density, measured as a function of time, is shown in Figure 3. The anodic current density of the films decreased with an increase in their fluorine content. The current density for the film prepared from pure acetylene is much higher than that for the film prepared from 10% acetylene and 90% HFE, suggesting that fluorine incorporation in the carbon film alters the film structure and properties in such a way as to reduce the solution uptake considerably.

Potentiodynamic measurements were also performed on some of these films by sweeping the applied potential from -2.0 to 2.0 V (SCE) at the rate of 5 mV/s and recording the resulting current density

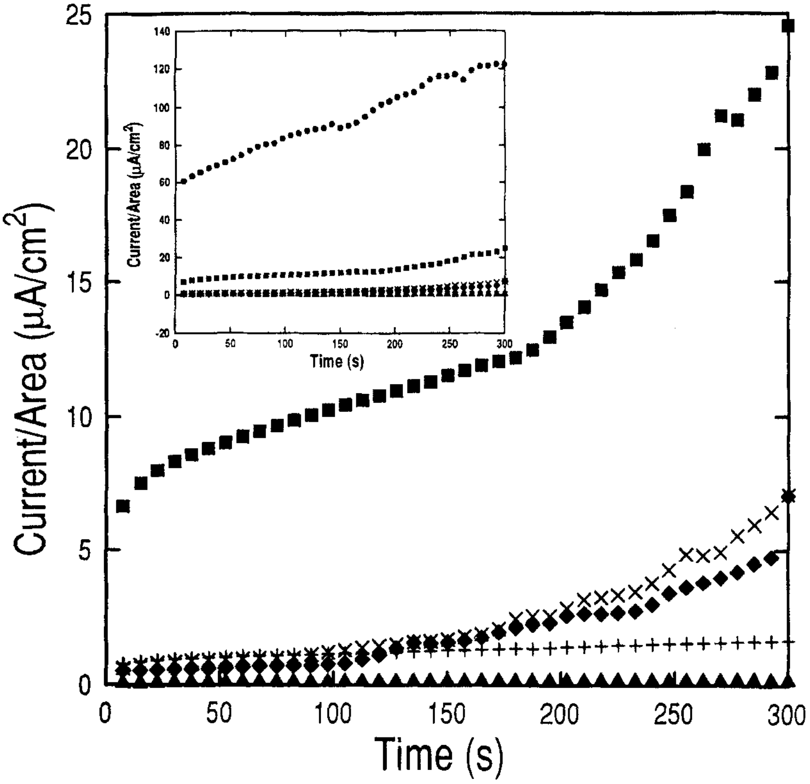

FIGURE 3 Anodic current density as a function of time for (▲) Ac/HFE-100, (+) Ac/HFE-90, (◆) Ac/HFE-70, (×) Ac/HFE-50, (■) Ac/HFE-25, and (●) Ac/HFE-0 (DLC); anodic current density for the DLC film-coated sample (●) is shown in the inset; the deposition conditions for all the films are given in Table I.

as a function of the applied potential. Figure 4 shows the polarization curves for a bare stainless steel sample and a fluorocarbon film-coated sample (Ac/HFE-100; see Tab. I). The critical current density for the coated sample is almost 4 orders of magnitude less than that for the bare sample and anodic dissolution sets in at a much more noble potential in the case of the coated sample compared with the bare sample. Also, the polarization curve for the bare sample shows active-passive transition while the curve for the coated sample does not show any such transition. All these features demonstrate the very good barrier properties of this fluorocarbon coating.

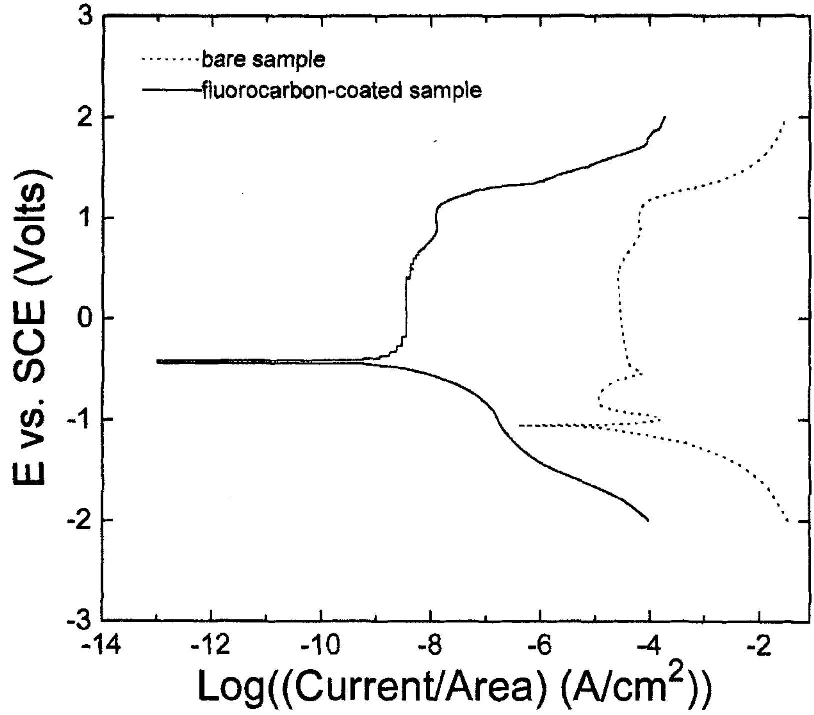

FIGURE 4 Polarization curves for bare and a fluorocarbon film-coated type 301 stainless steel substrates; the conditions for the deposition of the fluorocarbon coating (Ac/HFE-100) are given in Table I.

Electrochemical impedance spectroscopic (EIS) measurements were also carried out on these films and have been discussed elsewhere in greater detail [21]. The nearly-invariant EIS spectra for some of these films in the frequency range 10 MHz–4 KHz suggest that these films are free of any solution uptake.

CONCLUSIONS

Films were prepared from plasma polymerization of HFE and HFA fluorocarbon monomers with acetylene co-reactant gas. Their surface energies and surface compositions were characterized. The results demonstrated that the combination of the fluorocarbon monomer and hydrocarbon reactant gas gave polymerized thin films with surface energies that varied from 20 to 50 mN/m, depending on feed gas composition and processing parameters.

There was not much difference between the surface energies of the films prepared from HFE and HFA under otherwise identical process conditions. Variation of the fluorocarbon monomer/hydrocarbon ratio in the feed gas changed the amount of fluorine incorporated into the films and the distribution of fluorinated species in the films. Higher fluorine content in the films and lower surface energies were observed when the fluorocarbon monomer content of the feed gas was higher. Acetylene acted effectively as a fluorine scavenger in the materials studied here, permitting polymerization of HFE into fluorocarbon films.

The corrosion characteristics of a-C:H/fluorocarbon composite film structures, deposited from HFE/acetylene mixtures on type 301 stainless steel substrates, was studied using potentiostatic techniques. The anodic current density for these films was at least 3 orders of magnitude smaller than that for the bare stainless steel substrate. The resistance offered by these films to solution penetration increased with increasing fluorine content in the films.

Acknowledgements

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