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Surface properties of electrodeposited a-Si : C : H : F thin films by X-ray photoelectron spectroscopy

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Surface properties of amorphous silicon thin films containing hydrogen, flourine and carbon obtained from hydrofluosilicic acid and ethylene glycol using the electrodeposition method are reported as a function of current density and deposition time. The Si2p core level X-ray photoelectron spectra exhibited binding-energy shifts corresponding to SiF_x ($x=$ 1–4), SiC, Si–H and Si–O_2 type bond formations. The shifts in 1s spectra of fluorine, carbon and oxygen confirmed the presence of fluorine, carbon and oxygen in bonded form. Theoretical binding-energy shifts calculated from Pauling's electronegativity values were in close agreement with the measured values. The relative concentration values of C/Si estimated in these films were found to be larger than those of F/Si and O/Si. The results were corroborated with infrared spectroscopy and scanning electron microscopy data.

1. Introduction

Amorphous silicon (a-Si) and a-Si alloys containing hydrogen, fluorine and carbon, are important electronic materials with extensive applications [1–3]. Thin films of these materials were widely reported using glow-discharge decomposition (GDD), sputtering (SP) and chemical vapour deposition (CVD) methods [4–6]. Electrodeposition is a very simple, low-cost, and energy-efficient technique for making these films [7]. Silicon was deposited from a solution of SiF_4 in alcohol [8] and $SiCl_4$ in propylene glycol [9]. Amorphous silicon containing hydrogen was electrodeposited from a solution of $SiHCl_3$ in aprotic organic solvents such as propylene carbonate [10]. Takeda *et al.* [11] reported that a-Si could also be deposited cathodically from solutions of tetra orthosilicate in acetone or acetic acid. Ramamohan and Kroger [7] studied the cathodic deposition of a-Si with an electrolyte consisting of tetra ethyl orthosilicate dissolved in formamide–ethylene glycol mixture. Recently, studies on electrodeposited a-Si films using hydrofluosilicic acid (H_2SiF_6) and ethylene glycol were reported [12, 13].

In the pure state, a-Si contains dangling bonds which give rise to energy levels in the forbidden gap and make the doping practically difficult [4]. The dangling bonds can be removed by incorporating modifiers such as hydrogen, oxygen and fluorine [5, 14, 15] and hence the electrical properties can be easily changed by doping with suitable impurities. The type of bonds formed by incorporation of the modifiers can be determined by X-ray photoelectron spectroscopy (XPS) [16–18] and infrared spectroscopy (IRS) [6, 19]. The surface chemical structure of a-Si and a-Si alloy thin films is very important from the application point of view [20]. The properties of these films will depend on how the alloying elements, such as hydrogen, fluorine and carbon atoms, are placed in the a-Si network. Although a number of reports are available on electrodeposition of a-Si, so far no detailed studies have been carried out on the surface properties. This is also true with respect to the electrodeposited a-Si alloy films. We have earlier reported detailed studies on structural, morphological and infrared properties of the electrodeposited a-Si : C : H : F thin films [12, 13]. The electrical resistivity of these films was of the order of 10^{12}–10^{13} Ω cm [13]. In this paper we report an elaborate study on surface properties of a-Si films obtained by electrodeposition using an H_2SiF_6 and ethylene glycol electrolyte system. The results are corroborated with Fourier transform–infrared spectroscopy (FT–IR) and scanning electron microscopy (SEM) data.

2. Experimental procedure

In this study an electrolyte consisting of H_2SiF_6 and ethylene glycol was used. The films were deposited on

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stainless steel and indium tin oxide (ITO)-coated glass substrates. A rectangular platinum mesh was used as anode. The deposition was carried out at room temperature using a water bath. Several preliminary trials [21, 22] were conducted to deposit the films by varying the concentration of H_2SiF_6 in the electrolyte in the molar ratio 0.02–0.5 M at regular steps. At low concentrations, the deposition rate was observed to be very small. The film quality was badly affected at very high concentrations due to bubbling of the gases evolving at the cathode. At high concentrations, greater than 0.2 M, although the deposition rate was large, some loss in weight of the deposited material was observed. This phenomenon was attributed to some reverse reactions taking place in the electrolyte system during deposition. The deposition mechanism for these films was given elsewhere [12, 13]. It was confirmed that at 0.2 M concentration, the films obtained were of uniform nature with maximum possible thickness. Therefore, in the present study, the analysis was focused on the samples prepared at 0.2 M electrolyte concentration.

XPS spectra were recorded with a VG ESCA III Mark II spectrometer using an Al*K* source. The base pressure in the instrument was about 10^{-8} torr (1 torr = 133.322 Pa). Infrared spectra were obtained in the wave number region 400–4000 cm^{-1} using a Nicolet 170 SX FT–IR spectrometer. A high-resolution Siemens "Auto Scan" scanning electron microscope and a Phillips PW 1140 X-ray diffractometer were employed to obtain the structural and morphological data.

3. Results and discussion

Table I gives the preparation conditions of the samples used in this study. XPS spectra were recorded on the films deposited on stainless steel substrates. XRD results on the present films showed the amorphous nature, with no evidence of sharp peaks corresponding to silicon planes [13]. The thickness and electrical resistivity of these films lie in the ranges 9–10 μm and $1\text{–}2 \times 10^{12}$ Ω cm, respectively (Table I). The substrates were exposed on both sides during deposition. Therefore, the thickness of the films was measured on both sides of the deposition at different locations and the average values are reported here. The observed decrease in thickness and the change in electrical resistivity of the films for longer deposition times and higher current densities may be attributed, as mentioned above, to some reverse reactions taking place during deposition, and hence resulting in different chemical and physical structure in the films. The resistivity values in the present samples are an order of magnitude smaller than those reported by Ramamohan and Kroger [7] for electrodeposited a-Si films using a different electrolyte system.

XPS spectra give information on the core levels of silicon through binding-energy shifts. Typical Si2p spectra for samples deposited at different values of current density and deposition time are shown in Fig. 1. The spectra contained several unresolved peaks arising due to complexity of the electrodeposition system, owing to the participation of various types of bonds/species in the film formation. However, it is possible to explain the nature of the spectra with a prior knowledge of the deposition mechanism and the theory of chemical shifts. The observed binding energy shifts and the respective assignments for these shifts are given in Table II.

Fluorine is the most electronegative element and maximum binding-energy shift will be observed when bonded to silicon as compared to that in the case of Si–H, Si–C and Si–O bonding. In Fig. 1 the presence of SiF_x ($x = 1\text{–}4$) type species can be seen with a binding-energy shift corresponding to 100.89, 102.76, 104.79 and 106.63 eV, respectively [16–18]. When compared to the values of Ley *et al.* for sputtered a-Si : F films [17] the observed shifts in the present study are somewhat larger. This may be ascribed, as mentioned above, to the complexity of the film deposition process by the present method. Shimida and Katayama [18] and Gruntz *et al.* [16] reported the Si2p spectra for a-Si films with a binding-energy shift,

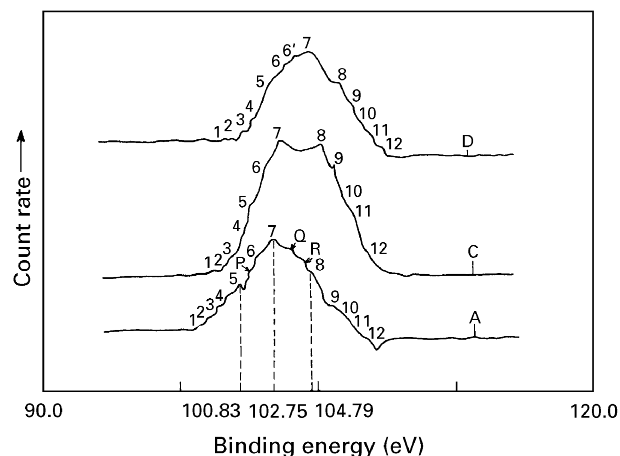

Figure 1 XPS spectra of samples A, C and D (Si 2p core level). Source AlK_α, voltage 12.5 kV, current 20 mA, energy 50 eV, slits 4 mm, time 300 s, counts 3×10^3 s.

TABLE I Sample specifications for surface studies

Sample	Molarity (M)	Deposition time (min)	Current density (mA cm^{-2})	Charge correction (eV)	Thickness (μm)	Electrical resistivity (10^2Ω cm)
A	0.2	120	100	+ 0.2	10.54	1.86
B	0.2	120	120	+ 0.4	10.35	1.93
C	0.2	180	100	− 0.5	9.83	2.17
D	0.2	180	120	− 1.1	9.62	2.45

TABLE II Observed binding-energy shifts (after charge correction)

Peak no.	Peak position (eV)			Assignment
	Sample A	Sample B	Sample C	
1	99.00	99.00	99.00	a–Si
2	99.45	99.44	99.25	Si–H
3	99.65	99.70	99.82	$Si–CH_3$
4	100.41	100.54	100.35	Si–C
5	100.89	100.90	100.89	Si–F
6	101.85	101.73	101.89–102.45	SiO_2
7	102.76	102.78	102.82	SiF_2
8	104.79	104.68	104.71	SiF_3
9	105.73	105.52	105.61	$H–SiF_4$
10	106.25	106.28	106.31	Si–OH
11	106.63	106.67	106.72	SiF_4
12	107.23	107.16	107.13	$HSiF_5$

Reference binding energies (eV): (a) Si 2p, 99.1 + 0.1; (b) F 1s, 686.2 + 0.1; (c) O 1s, 532.0 + 0.1; (d) C 1s, 284.6 + 0.1. All energies are relative to E_F, taken from [6, 25].

TABLE III Relative concentration ratios

Sample code	Relative concentration		
	C/Si	F/Si	O/Si
A	0.34	0.15	0.155
B	0.39	0.156	0.15
C	0.46	0.15	0.16
D	0.56	0.14	0.15

E(F) = 1.15 and 1.2 eV, respectively, for each atom of fluorine bonded. In the present study, the E(F) value was observed to be approximately 1.89 eV. This larger value may be due to high concentration of F/Si in the electrodeposited films (Table III).

From the above figure it is evident that the concentration of SiF_2 and SiF_3 species is high compared to that of SiF_1 and SiF_4 species. Further, the number of SiF_4 units is small for all samples while the intensity of SiF_1 configuration is high in sample A at 100.89 eV. Ley *et al.* [17] observed that for concentrations of fluorine (14%) in sputtered samples, the density of SiF_1 type units was high. With increased fluorine concentration, the SiF_2 and SiF_3 configurations became predominant while the contribution of SiF_1 decreased relatively. It was also stated that SiF_4 clusters were observed only at fluorine concentrations higher than 40 at% [17]. In the present study, the SiF_2 and SiF_3 units were observed to exist in relatively large numbers for samples deposited at higher current density and longer deposition time.

Si–H shift was observed in the present spectra at 99.25–99.45 eV [20, 23, 24]. The spectra also showed binding-energy shift corresponding to four-fold carbon bonding at 100.35–100.54 eV [20, 25]. The presence of SiO_2 can be seen at 101.85 eV [20, 23, 25, 26] and the region marked "P" (sample A) is due to the presence of SiO_2 in different back-bonded environments. According to the reaction mechanism [12, 13], some intermediate species like $HSiF_3$, $HSiF_4$ and

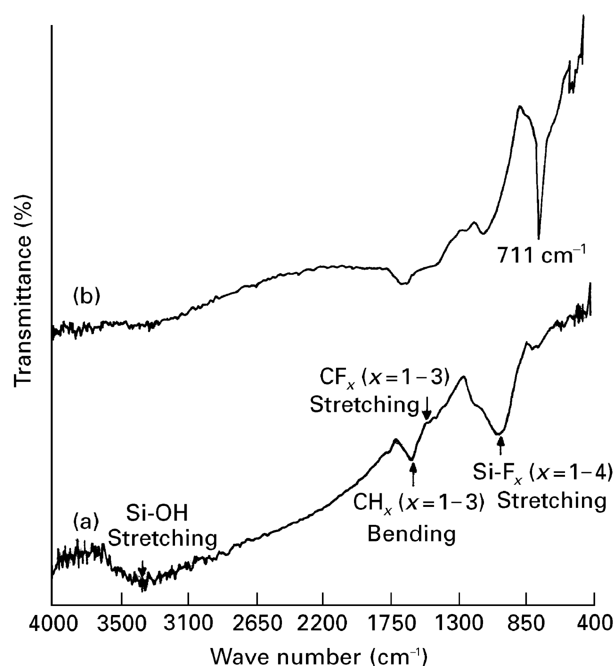

Figure 2 FT–IR spectra of samples deposited at (a) 0.05 M, 30 mA cm^{-2} and (b) 0.2 M, 120 mA cm^{-2} (400–4000 cm^{-1}).

$HSiF_5$, could be formed with shifts observable at higher binding energies (Table II). The hump "Q" has been tentatively assigned to the presence of $HSiF_3$.

We have reported that ethylene glycol also interferred with the film-deposition process [12]. This gives the possibility of CH_3 and CF_3-type species being present in the films. The electronegativity of CF_3 is 3.35 with an effective charge of 0.45 eV. This leads to a change in binding energy of about 1.215 eV when singly bonded to silicon. Therefore, the shift in the region "R" indicates the possible presence of CF_3 in four-fold coordination. The absorption peaks for these species are clearly seen in FT–IR spectra at 1250–1450 cm^{-1} (Fig. 2). The $CH_x(x = 1 - 3)$ bending mode is centred at around 1590 cm^{-1}. The intense stretching mode of the same species is presumably merged into the strong and broad absorption from 2800–3600 cm^{-1} which also arises due to the presence of Si–OH type bonding in the films [12].

Theoretical binding-energy shifts (Table IV) for various types of bonds present in the films have been calculated using Pauling's electronegativity values and the procedure given elsewhere [6, 26–29]. In these calculations, we have taken the value of β as 2.7. β is a proportionality factor and is inversely related to the valence shell radius. Table V gives a comparison of the observed shifts with other reported values for a-Si alloy films obtained by other deposition methods. The discrepancy in the present values can be understood in terms of the complex nature of the electrodeposition process during film formation.

The 1s spectra of fluorine, carbon and oxygen are shown in Figs 3–5. The corresponding energy shifts are given in parentheses in Table VI. These shifts, in turn, confirm the presence of oxygen, fluorine and carbon in bonded form. The 1s spectrum of oxygen (sample D, Fig. 5) clearly shows two unresolved peaks

TABLE IV Calculated binding-energy shifts

No.	Element/ species	Electro negativity	Nature of the bond	Effective charge (Δq)	Binding energy shift (eV)
1	Si	1.8	–	–	–
2	F	4.0	Si–F	0.7	1.89
3	O	3.5	Si–O	0.514	1.39
4	C	2.5	Si–C	0.115	0.31
5	H	2.1	Si–H	0.022	0.06
6	OH	3.5–3.9	Si–OH	0.51–0.67	1.28–1.81
7	CH_3	2.3	Si–CH_3	0.06	0.16
8	CF_3	3.35	Si–CF_3	0.45	1.22

TABLE V Comparison of observed BE shifts with other reported values

No.	Species	Observed BE shifts (eV)	Other experimental BE shifts (eV)	Film	Method	Reference
1	SiF	100.89–100.90	(a) 100.75 + 0.1	a-Si:F	SP	[16, 17]
			(b) 100.8 (99.6 + 0.1)	a-Si:F	GD	[18]
2	SiF_4	106.63–106.72	104.42 + 0.1 (99.6 + 0.1)	a-Si:F	SP	[16, 17]
3	SiH	99.25–99.45	(a) 98.15 (98.3)	a-Si: H	SP	[23]
			(b) 98.65 (98.8)	a-Si: H	SP	[20]
			(c) 99.2	a-Si: H	GD	[24]
4	SiC	100.35–100.54	(a) 99.2-101.1	a-Si_x:C_{1-x}: H	GD	[25]
			(b) 98.9-101.0	a-Si_x:C_{1-x}: H	SP	[20]
5	SiO_2	101.73–102.45	(a) 102.0 (98.3)	a-Si:H	SP	[23]
			(b) 102.5 (99.25)	a-Si:C: H	GD	[26]
			(c) 102.8	a-Si_x:C_{1-x}:H	GD	[25]
			(d) 102.0	a-Si_x:C_{1-x}:H	SP	[20]

SP, sputtering; GD, glow discharge; BE, binding energy.
Values in parentheses are the reference BE values for Si 2p level.

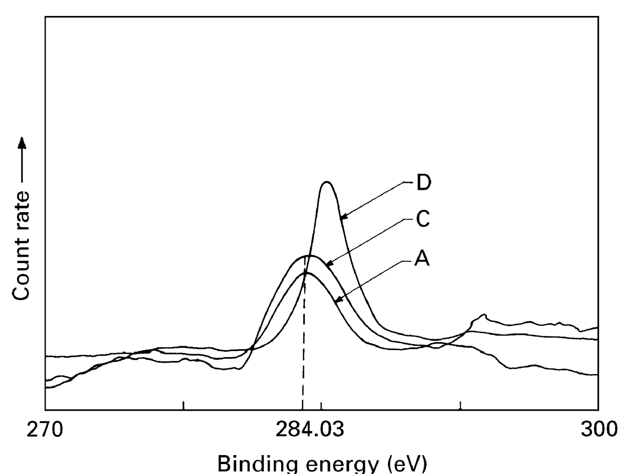

Figure 3 1s spectra for samples A, C and D. Details as in Fig. 1.

TABLE VI 1s Core level positions of carbon, fluorine and oxygen (after charge correction)

Sample code	Peak positions (eV)		
	C	F	O
A	284.32 (0.28)	685.52 (0.68) 685.93 (0.27)	529.94 (2.06)
B	284.24 (0.36)	685.72 (0.48)	530.22 (1.78)
C	284.48 (0.12)	685.92 (0.28)	530.89 (1.11)
D	284.08 (0.52)	683.81 (2.39)	530.08 (1.92)

Values in parentheses are BE shifts relative to reference values given as footnotes to Table II.

indicating the presence of oxygen in different chemical states. Correspondingly, the Si 2p spectrum of sample D (Fig. 1) also exhibited two peaks (6 and 6′) at 101.89 and 102.45 eV, due to SiO_2 in different back-bonded environments.

The relative concentrations of carbon, fluorine and oxygen with respect to silicon are given in Table III [6]. It is seen from the table that C/Si values are very high compared to those of F/Si and O/Si. The high values of C/Si can lead to some serious implications in the structure of the deposited films [26]. The fairly large relative intensity values indicate that the deposited films are heavily alloyed [6].

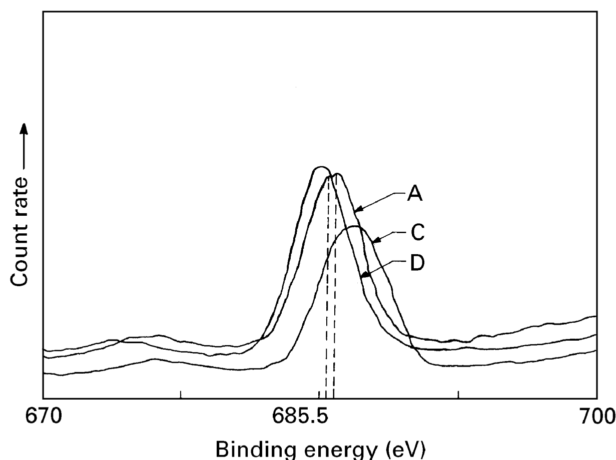

Figure 4 F 1s spectra for samples A, C and D. Details as in Fig. 1.

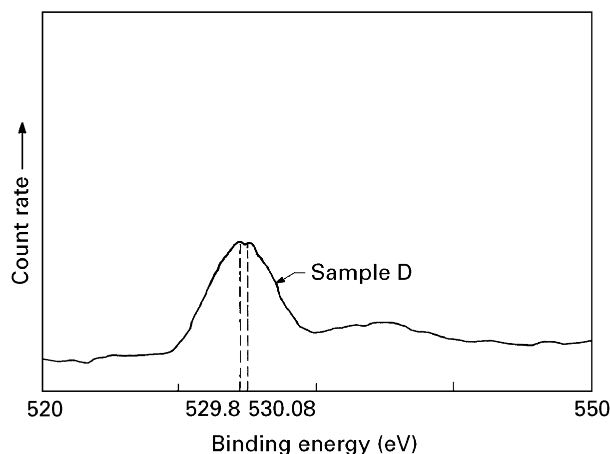

Figure 5 O 1s spectra for sample D. Details as in Fig. 3.

Similar results are observed for sample B (spectra not shown). It is also worth mentioning here that Gruntz *et al.* [16] reported the possibility of some less-likely configurations, such as $(SiF_2)_n$ or coupled SiF_n units, being present in the sputtered a-SiF films. However, it was expressed that the presence of such entities will have to be established by means other than photoemission [16]. A detailed analysis of FT–IR and SEM data on electrodeposited samples used in the present study revealed that no such polysilane formations were present in the films. This can be stated by considering (a) the absence of doublets (paired frequencies) in the wave number region corresponding to SiF stretching, and SiH bending absorption modes [30, 31] in Fig. 2, and (b) the absence of diphasic character that represents a columnar growth [6, 32, 33] in scanning electron micrographs (Fig. 6).

Infrared spectra provide valuable information on the nature of chemical bonding in the deposited material. The vibrational modes and their assignments given in Fig. 2 support the above XPS analysis. At low electrolyte concentrations (Fig. 2a) the film is rich with Si–F and Si–OH bonds. The presence of hydroxyl groups could not be a positive factor regarding the quality of the films [6]. At high concentrations (Fig. 2b), the Si–OH absorption is completely absent but the Si–F absorption modes have also decreased

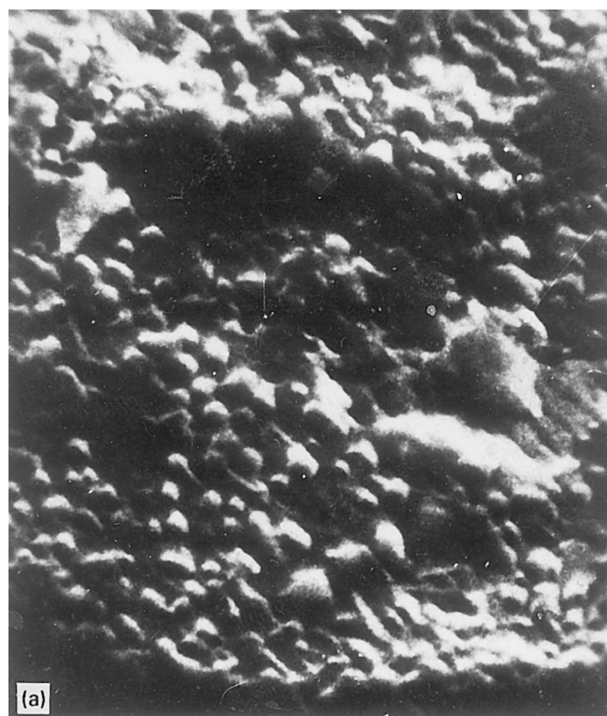

Figure 6 Scanning electron micrographs of the electrodeposited samples (X 25 000): (a) 0.05 M, 30 $mA\,cm^{-2}$, and (b) 0.2 M, 120 $mA\,cm^{-2}$.

considerably. There is a strong absorption peak at 711 cm^{-1} due to Si–C stretching vibrations. Borders *et al.* [19] also observed a single absorption band centred at 700 cm^{-1} in carbon-implanted a-Si due to triply degenerate bond-stretching vibrations of the carbon atom. However, the corresponding XPS spectrum (sample D) shows only a less intense feature in the region corresponding to Si–C shift. This indicates that most of the Si–C bonds are present in the bulk of the specimen rather than at the surface. The scanning electron micrograph of sample D (Fig. 6b) exhibited

a homogeneous structure which appeared to be similar to that reported on a-Si films obtained by sputtering and glow-discharge decomposition methods [6, 18]. The dark and lightly shaded regions correspond to different density environments of the deposit. As mentioned above, the absence of columnar projections in this micrograph correlates with the absence of polysilane conformations in electrodeposited films [6, 32, 33]. Details of the fracture surface were given elsewhere [13].

4. Conclusion

The surface properties of thin films of silicon electrodeposited on stainless steel substrates were investigated. Analysis of XPS and FT–IR data showed that Si–F, Si–H and Si–C type bonds were present in the films in varying intensities. Therefore, the deposited material is not pure a-Si and can best be termed an a-Si alloy (a-Si:C:H:F). Morimoto *et al.* deposited the a-Si:C:F:H films using a glow-discharge decomposition method [34]. These amorphous silicon–carbon alloys are reported to have a wide optical gap with applications in photovoltaic and luminescent devices [35, 36]. The present studies revealed that the chemical nature of the films is largely dependent on the deposition parameters. At high electrolyte concentration, the films comprise intense Si–C bonds, while at low concentrations Si–OH units are present in high intensity. XPS studies provided evidence for $Si–F_1$, $Si–F_2$, $Si–F_3$ and $Si–F_4$ type species existing as separate entities. Further studies of deposition on other metallic substrates would be useful in further understanding the surface chemical nature of the electrodeposited films and also to check the extent of interference from ethylene glycol in this process.

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