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Supplementary material

X-ray photoelectron spectroscopy was used to determine the chemical composition of silica films deposited using the FlexAL tool. The peaks were fitted using pseudo-voigt1 shape function (linear combination of Gaussian-Lorentzian) (equation 1) in OriginPro2017 software (Northampton, USA).

$$y = y_o + \left[\frac{2wm_\mu}{\pi} \frac{1}{4(x - x_c)^2 + w^2} + \frac{(1 - m_\mu)\sqrt{4ln2}e^{a}}{\sqrt{\pi}w} \right] \quad (1)$$

$$a = -\frac{4ln2}{w^2}(x - x_c)^2$$

Here y_0 is offset, X_c is center, A is area, w is full width half maximum (FWHM) and m_μ is a profile-shape factor. The iteration for the fit was performed until the function converged and chi-square tolerance value was reduced to 1E-9. The constraints during the fit were applied on profile shape factor ($0 \le m_\mu \le 1$) and FWHM ($W > 0$). Shirley baseline correction was performed for all peaks. To fit C 1s spectra, m_μ for the peak corresponding to C-C bonded carbon was shared with the peaks corresponding to C-O=C and C-O. Figures S1-S4 show peak fitting of high-resolution spectra corresponding to Si 2p, O 1s and C 1s for SiO_2 films deposited with 0 V, -111 V, -206 V and -295 V, respectively, using the FlexAL tool. The area under the peak and binding energies of Si 2p, O 1s, and C 1s are summarized in Table S1 and S2. The O/Si ratio was calculated using equation 2:

$$\frac{O}{Si} = \frac{(Area\ O\ 1s_{\ o-si} + Area\ O\ 1s_{chemisorbed})/ASF_O}{Area\ Si\ 2p/ASF_{Si}} \quad (2)$$

where atomic sensitivity factor (ASF) for the Si 2p is 0.34 and for the O 1s is 0.71

Figures S1 - S4 show high-resolution spectra of Si 2p, O 1s and C 1s respectively, of the films deposited using average-bias voltages of 0 V, -111 V, -206 V and -295 V using the FlexAL tool (see table S2). The shift in the peak position was observed due to static charging of the samples. Hence, a C 1s peak position at 284.8 eV corresponding to adventitious carbon was considered as a reference for correcting shifts in the peaks.[1-3] Fig S1a, S2a, S3a, and S4a shows the Si 2p spectra fitted with a single peak. The O 1s spectra shown in Fig. S1b, S2b, S3b, and S4b are deconvoluted into two peaks. The major O 1s peak at lower binding energies corresponds to Si-O bonding.[4] The minor O 1s peak at higher binding energy corresponds to physisorbed water.[5, 6] C 1s spectra shown in Fig. S1c, S2c, S3c, and S4c are deconvoluted into three peaks. The major peak at lower binding energy corresponds to C-C adventitious carbon, mostly present on the surface.[7] The two minor peaks at lower binding energies correspond to C-O, and O-C=O carbon groups present in the thin film.[1-3] It is important to note that although the O-1s spectrum is fitted with two peaks, the uncertainty in the fit of the area under peaks for all films (deposited using the FlexAL tool) at 534.6 eV is high (up to 25 %). Similarly, uncertainty in the fit of C- 1s peak at 289.0 eV is also high (up to 45 %).

The O/Si ratio calculated from XPS spectra of the SiO_2 film surface deposited without substrate biasing using the FlexAL tool is 1.68 ± 0.05 (see Table S1). On increasing average-bias voltage, the XPS spectra of SiO_2 films shows nearly constant value. The low O/Si ratio of ~1.50 on the surface of SiO_2 films

determined from AES is in agreement with the low O/Si ratio determined from surface XPS measurement (see Table 5).

Table S1 The area under the high-resolution deconvoluted Si 2p, O 1s, and C 1s peaks determined from XPS and calculated O/Si ratio.

Average-bias voltage	**Area under the peak Si 2p**	**Area under the peak O 1s**		**Area under the peak C 1s**			**O/Si**
V	(± 3 %)	O-Si (± 5 %)	$O_{chemisorbed}$ (± 25 %)	C-C (± 11 %)	C-O=C (± 20 %)	C-O (± 45 %)	(± 0.05)
0	28299	76926	22907	4226	406	130	1.68
-111	39125	97367	34466	5699	1278	305	1.61
-206	37009	85159	38438	3625	1810	27	1.59
-295	29044	67210	35155	3091	1758	80	1.68

Table S2 Binding energies (B.E.) of high-resolution spectra of Si 2p, O 1s, and C 1s. The SiO_2 films were deposited without and with substrate biasing in FlexAL tool.

Average-bias voltage	**B.E. (eV) Si 2p**	**B.E. (eV) O 1s**		**B.E. (eV) C 1s**		
V	(± 0.01)	O-Si	$O_{chemisorbed}$	C-C	C-O=C	C-O
0	103.61	533.32 ± 0.02	534.16 ± 0.05	285.27 ± 0.03	287.12 ± 0.18	289.00 ± 0.35
-111	103.60	533.02 ± 0.02	533.82 ± 0.04	285.18 ± 0.04	286.85 ± 0.14	289.58 ± 0.12
-206	103.47	532.75 ± 0.02	533.49 ± 0.02	284.86 ± 0.06	285.80 ± 0.10	289.53 ± 0.33
-295	103.56	533.12 ± 0.02	533.83 ± 0.03	285.14 ± 0.07	286.29 ± 0.10	289.49 ± 0.16

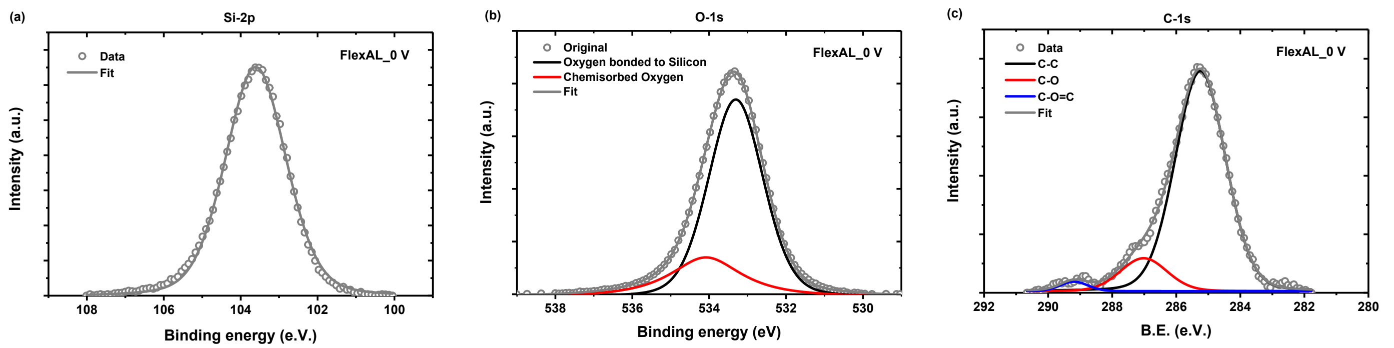

Fig. S1 The high-resolution spectra of SiO_2 film (a) Si 2p (b) O 1s (c) C 1s determined from XPS for the film deposited without bias using the FlexAL tool.

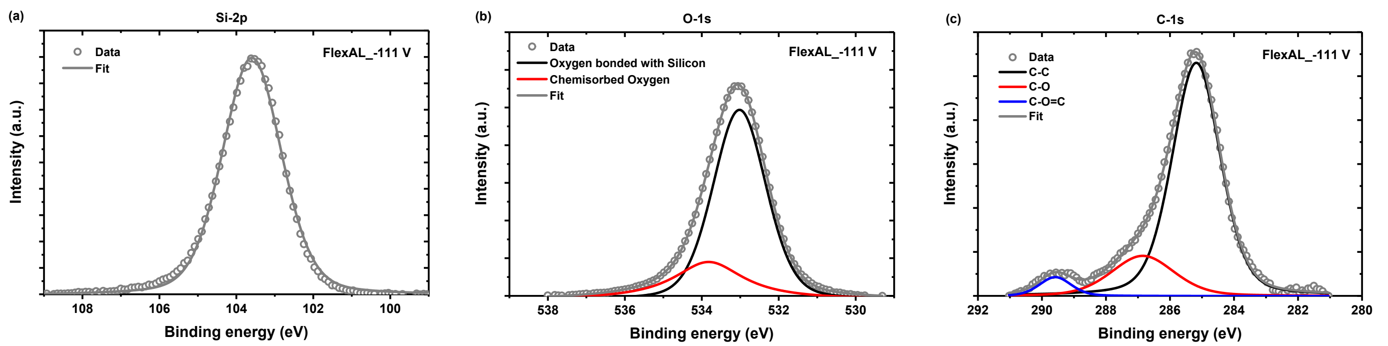

Fig. S2 The high-resolution spectra of SiO_2 film (a) Si 2p (b) O 1s (c) C 1s determined from XPS for the film deposited with -111 Vbias using the FlexAL tool.

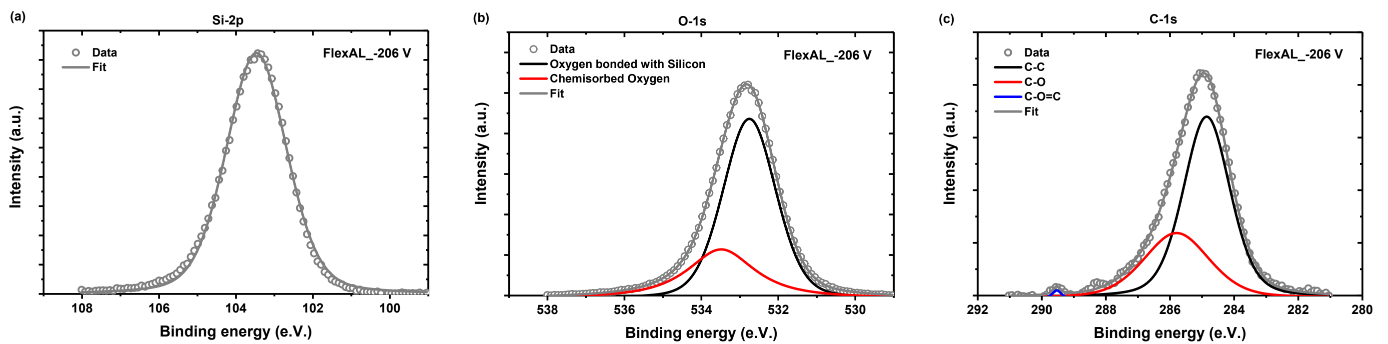

Fig. S3 The high-resolution spectra of SiO_2 film (a) Si 2p (b) O 1s (c) C 1s determined from XPS for the film deposited with -206 Vbias using the FlexAL tool.

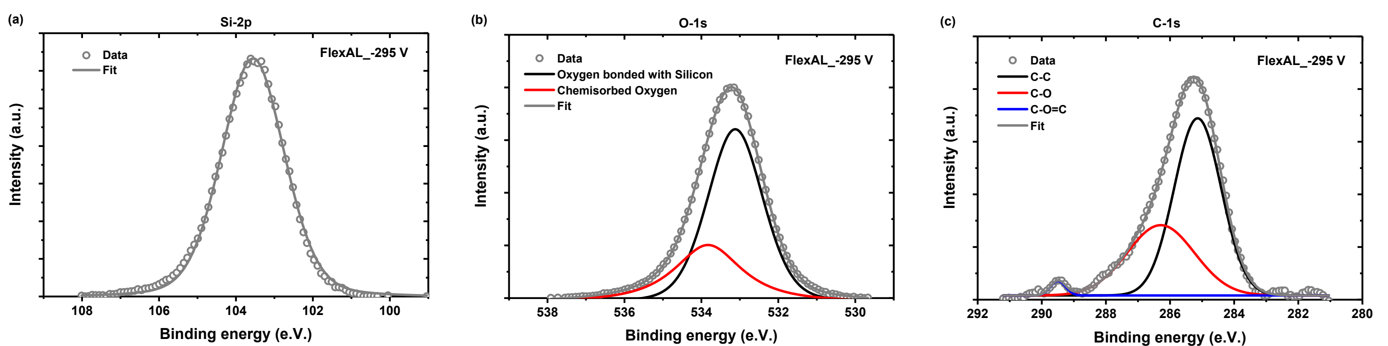

Fig. S4 The high-resolution spectra of SiO_2 film (a) Si 2p (b) O 1s (c) C 1s determined from XPS for the film deposited with -295 V bias using the FlexAL tool.

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