

Electronic Supplementary Information

Origins of Conductivity Improvement in Fluoride-Enhanced Silicon Doping of ZnO Films

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I. Additional Experimental Information:

Film Deposition

The basic procedure for the spray pyrolysis deposition of SiZO thin films is as previously described.¹ A desired quantity of ammonium fluoride (Sigma-Aldrich, 99.99+% metals basis) was added to a prepared base precursor solution of zinc acetylacetonate and (optionally) silicon tetraacetate. All additive/dopant amounts are reported as at% of the total metal and metalloid concentration (including Zn and Si) in the solution, which is kept constant at 0.15 M throughout this study. Films were deposited at a nominal substrate surface temperature of 376 °C.

We have compared the results for solutions prepared in glassware and those prepared entirely in plasticware and found no statistically significant difference in the properties of the resulting films in cases where silicon is added intentionally as silicon tetraacetate. Thus, the reported properties for films deposited from solutions containing intentionally added silicon are an average including samples deposited from solutions prepared in both plastic and glass laboratory ware. In the manuscript, results for films deposited from precursor solutions containing fluoride *without* added silicon are of those prepared using plastic labware only. A comparison of precursor solutions prepared in glass and plastic without added silicon is made in §2 of this supplementary information.

General Film Characterisation

Electrical transport measurements were performed by the van der Pauw method using an Ecopia HMS-3000 Hall effect measurement system with a 0.55 T permanent magnet.² Indium solder was used to create Ohmic electrical contacts of minimum size on the corners of approximately 5 mm x 5 mm pieces cut from larger deposited films. Where shown, error bars indicate the standard deviation in a property across a population of samples.

Optical transmission spectra were recorded between 250 and 2500 nm using a Perkin-Elmer Lambda19 UV-Vis-NIR spectrophotometer. Film thicknesses were estimated by applying the envelope method of Swanepoel to the low oscillation frequency interference fringes in the transmission spectrum.³ The higher frequency oscillations in the near IR result from internal reflections in the glass substrate. Reported optical transparencies are an average over the visible range (450-700 nm) with the effect of interference fringes removed, and corrected for the glass substrate (*i.e.*, the raw transmittance of the substrate-film assembly is divided by 0.92 to account for the 92% transparency of the bare glass substrate in this spectral range).

X-ray diffraction measurements were performed using a PANalytical X'Pert PRO diffractometer with Bragg-Brentano geometry and a fixed X-ray source at an emission current of 40 mA and an anode voltage of 45 kV. The spectra were recorded using monochromated Cu-K_{α1} radiation ($\lambda = 1.54059 \text{ \AA}$) over a time of 115 minutes. Samples were placed on a 60 rpm spinner during data collection to improve averaging of crystallite orientation.

II. Comparison of ZnO Samples Prepared from Fluoride-Containing Precursor Solutions in Glass and Plastic Containers:

In order to demonstrate the influence of the type of laboratory ware used to handle precursor solutions on the properties of the resulting ZnO thin films, two series of precursor solutions containing various amounts of ammonium fluoride and no intentionally added silicon were prepared and used to deposit ZnO thin films by spray pyrolysis. The two series were nominally identical except for the fact that one was prepared and handled in conventional glass laboratory ware, and the other series was handled exclusively using plastic implements without substantive silicon content.

The electrical conductivities of films in the two series are shown in Figure S2-1. For the series prepared in glassware, we find the conductivity is positively correlated with the fluoride concentration of the precursor solution, as has been previously reported by several other groups.⁴⁻⁶ However, there is no statistically significant change in the electrical conductivity with precursor solution fluoride concentration for the series handled in plastic.

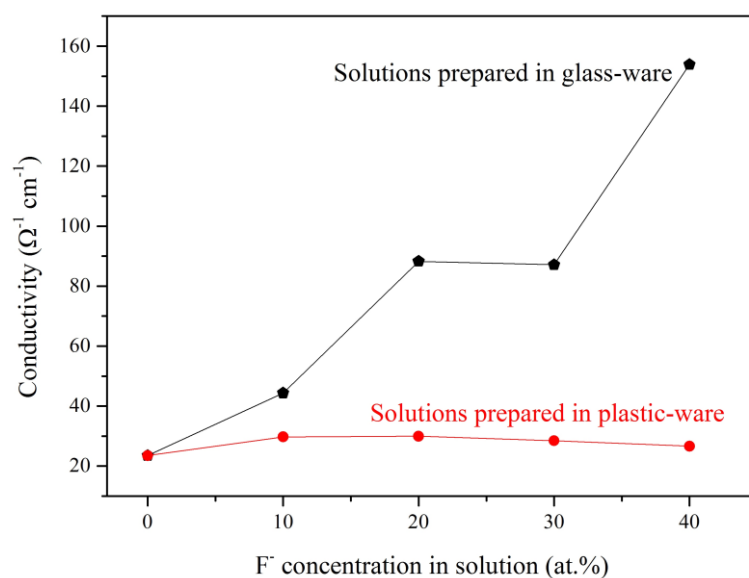


Figure S2-1 Electrical conductivity of ZnO thin films prepared from precursor solutions containing varying amounts of ammonium fluoride and no intentionally added silicon. Data are from samples where the precursor solution is prepared in glassware (black) and where the precursor solution is prepared in plasticware (red).

Figure S2-2 shows the carrier concentration and mobility as measured by Hall effect for films in these two series. Across the samples handled with plasticware, no significant changes are observed in either of these transport parameters with increasing precursor solution fluoride concentration. In contrast, the series of solutions handled in glassware without special precautions shows a substantial increase in carrier concentration and decrease in mobility that can be attributed to the introduction of electrically active defects.

This behavior is inconsistent with the model that fluoride is by itself acting as a dopant, and instead indicates that some aspect of the sample container (i.e., the experimental variable in this case) is leading to the observed conductivity increase. Based on the experiments described in the main article and in §3 of the Supplementary Information, this aspect appears to be the extraction of silicon (and potentially other components) from the glass by the action of aqueous fluoride.

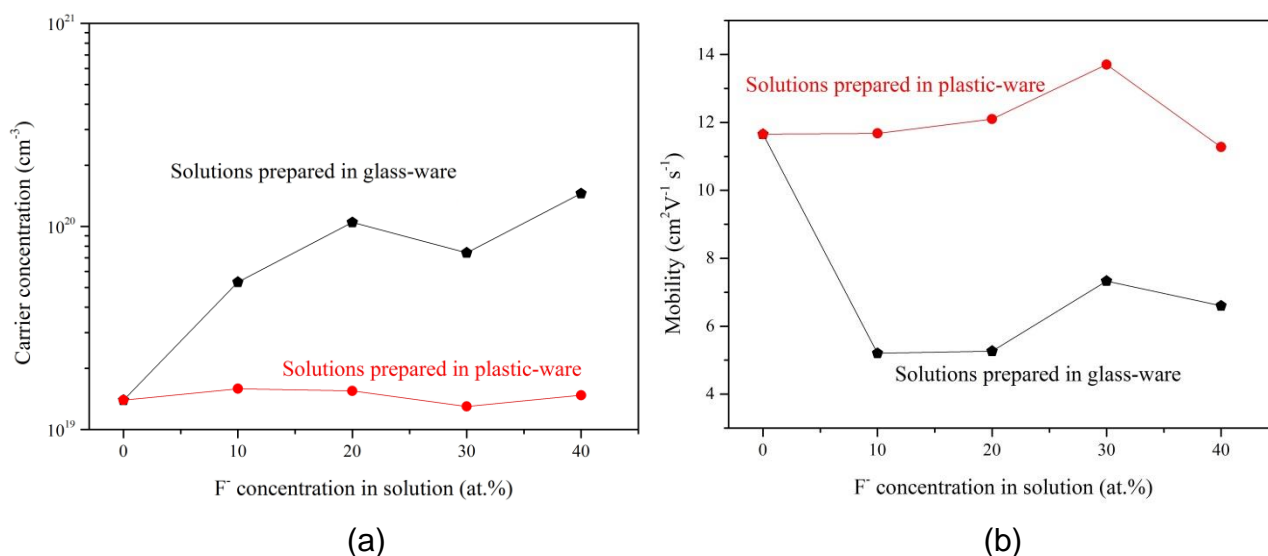


Figure S2-2 Hall effect carrier concentration (a) and carrier mobility (b) of ZnO thin films prepared from precursor solutions containing varying amounts of ammonium fluoride and no intentionally added silicon. Data are from samples where the precursor solution is prepared in glassware (black) and where the precursor solution is prepared entirely in plasticware (red).

III. NMR Study of Model Precursor Solutions

Proton-decoupled ¹⁹F NMR (376.50 MHz) spectra were recorded on a Bruker AVIII400 Nanobay spectrometer at room temperature. Samples containing 3:1, 12:1, and 1:0 molar ratios of ammonium fluoride and silicon tetraacetate (Aldrich, 98%) were dissolved in a mixture of acetic acid (Fisher Scientific, Analytical Reagent Grade), deuterium oxide (Apollo Scientific Limited, 99.92 at%D), and ethanol (Sigma-Aldrich, absolute, ≥99.8%) in a 7:93:200 volume ratio designed to simulate the spray pyrolysis solvent, except with water replaced by deuterium oxide to assist in locking of the spectrometer and to provide an internal frequency reference. Chemical shifts are measured based on the deuterium lock frequency, and are reported relative to CFC1₃. Unless otherwise noted, solutions were handled in plastic labware and FEP NMR tube liners (Wilmad) were used to prevent interaction of the solutions with the glass NMR tubes.

Monitoring over time revealed that the mixtures had largely reached equilibrium within the 30–40 minutes after preparation, with only very minor changes thereafter.

Fluoride participating in the F⁻/HF equilibrium is known to have a highly pH dependent chemical shift ranging from $\delta = -162$ to -120 ppm in aqueous solutions.⁷ The appearance of fluoride signals at $\delta = -135.5$ to -130.9 across the series are consistent with variations in pH from approximately 3.2 to 3.5 caused by changes in solute concentrations. The signal appearing at $\delta = -129.1 \pm 0.1$ ppm is assigned as that of the SiF₆²⁻ ion. When an ammonium fluoride solution (initially silicon free) comes into even brief contact with glass, the SiF₆²⁻ signal is observed in the resulting NMR spectrum, suggesting that chemical attack of the glass by the precursor solution is

occurring. The SiF_6^{2-} signal is of significant intensity if the fluoride containing solution is prepared using glassware, or if unlined glass NMR tubes are used for the analysis.

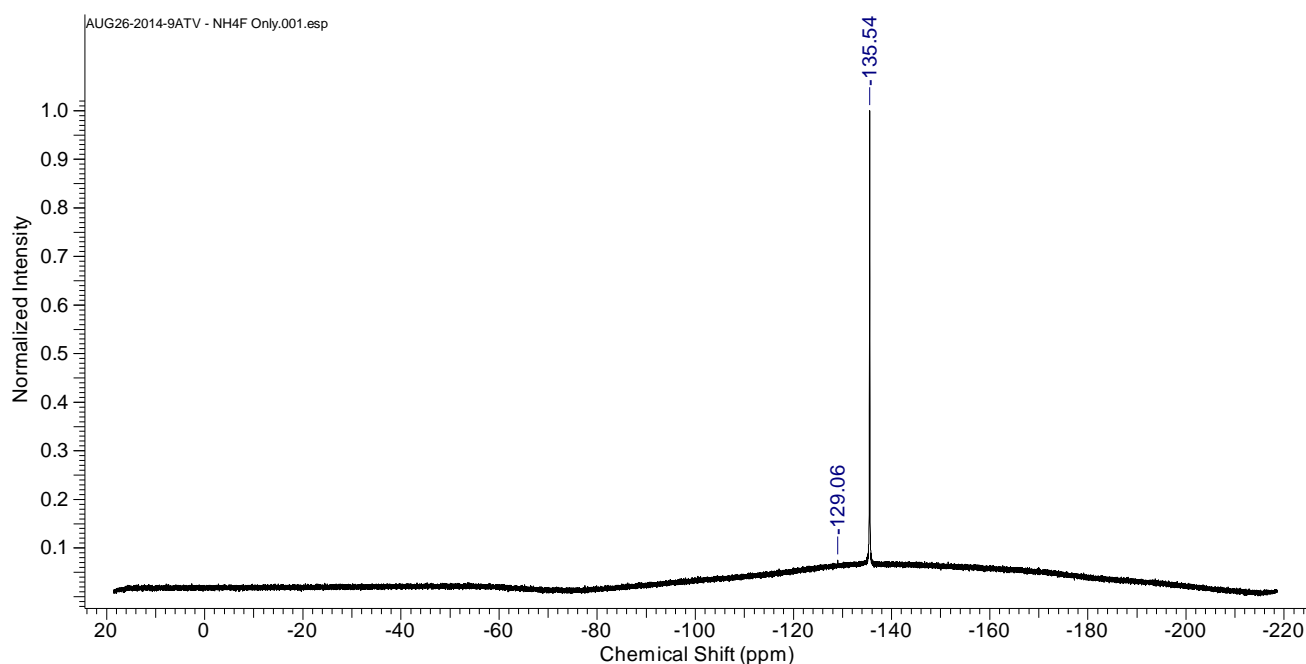


Figure S3-1 ^{19}F NMR of NH_4F in 2:1 ethanol:7 vol% acetic acid in D_2O (control experiment). The small impurity at $\delta = -129.06$ ppm is likely due to SiF_6^{2-} formed by inadvertent contact of the solution with a glass implement during sample preparation.

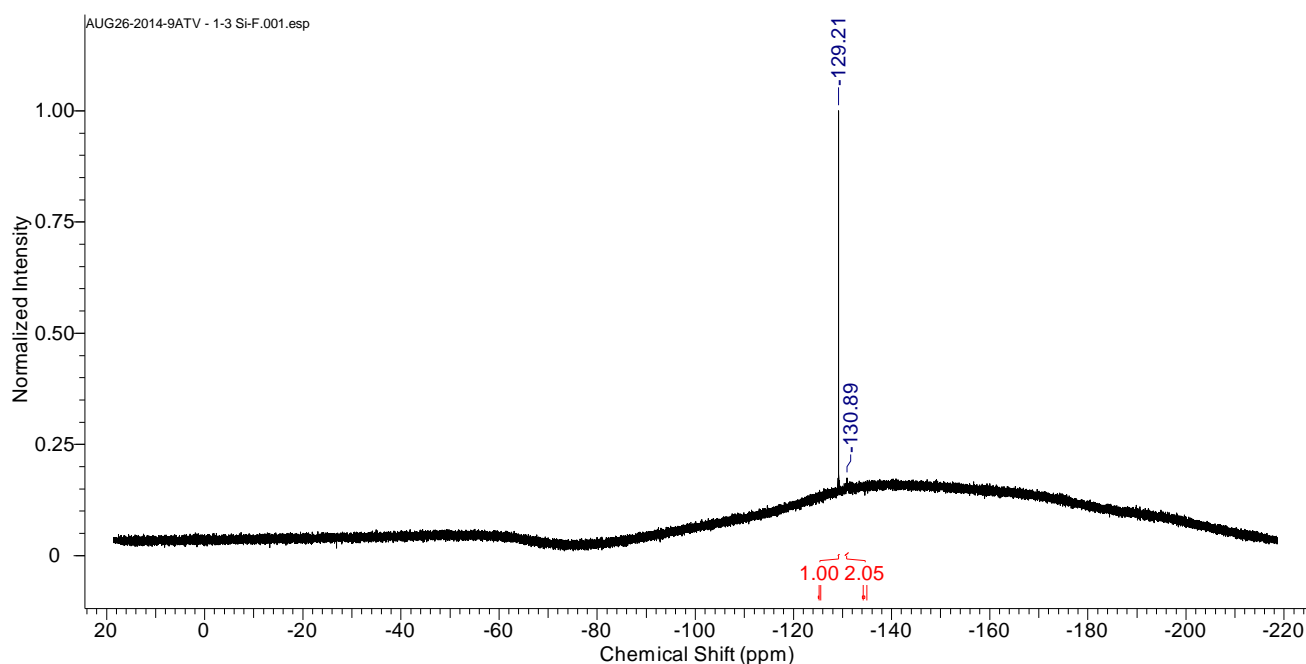


Figure S3-2 ^{19}F NMR of a 3:1 molar ratio of ammonium fluoride to silicon tetraacetate (excess of silicon) in 2:1 ethanol:7 vol% acetic acid in D_2O .

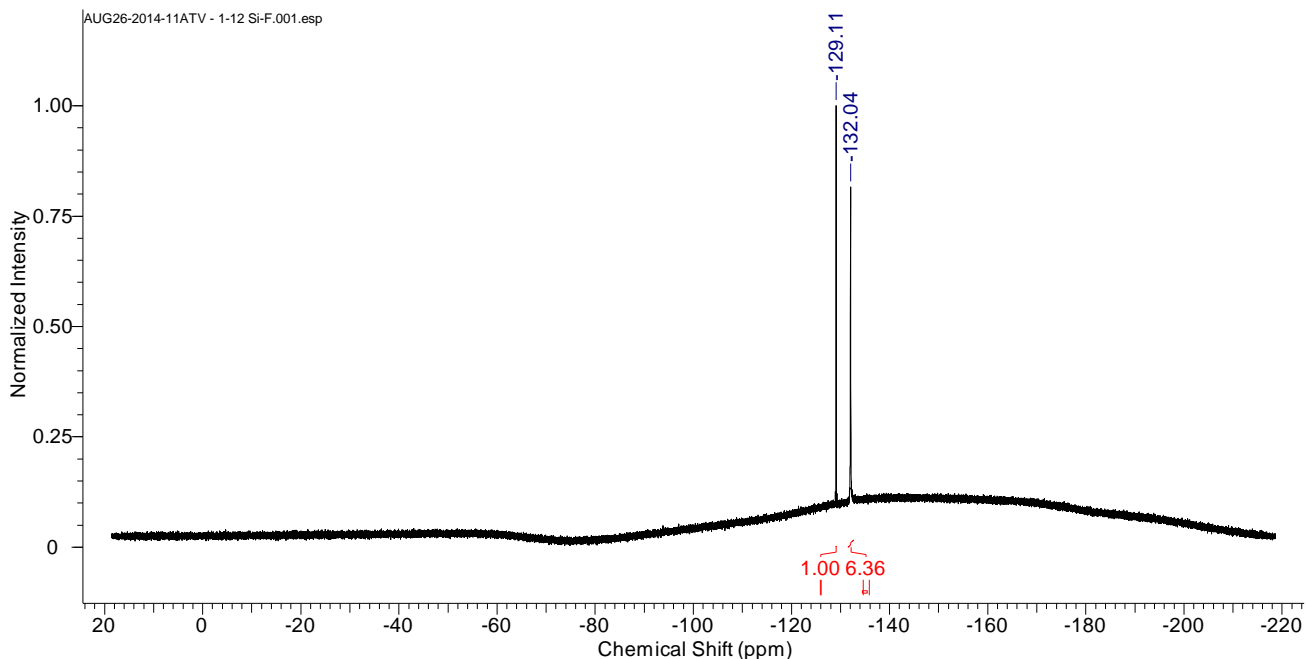


Figure S3-3 ^{19}F NMR of a 12:1 molar ratio of ammonium fluoride to silicon tetraacetate (excess of fluoride) in 2:1 ethanol:7 vol% acetic acid in D_2O .

IV. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) data were collected on a Thermo Scientific K-Alpha XPS with an $\text{Al-K}\alpha$ X-ray source (1486.7 eV). All spectra were acquired with a 0.4 mm diameter X-ray spot size and with charge compensation. The polished (111) surface of a phosphorus-doped silicon wafer (Pi-KEM, Ltd.) was used as a reference sample. Spectra were recorded from *as received* samples, as well as after ~600 seconds of etching using 4 keV argon ions from an MAGCIS ion source.

The Si:Zn ratio in these samples was determined by examining the average of 10 high resolution scans over a binding energy range of 110 to 75 eV, which includes the Si(2p) and Zn(3p) signals. The Si(2p) signal is centred at ~102.9 eV, while the Zn(3p) signal consists of 2 broad peaks centred at ~92.3 and ~89.5 eV, corresponding to the spin-orbit split $3p_{3/2}$ and $3p_{1/2}$ resonances, respectively. Using the CasaXPS software package, the peak areas were integrated using a linear baseline and normalised by the relative scattering factors tabulated in the default Scofield Element Library (0.817 for Si(2p) and 2.83 for Zn(3p)) to calculate the Si:Zn ratio (Figure S4-1). Two series of SiZO films were studied in this way. The first was prepared from solutions containing 3 at% Si and fluoride concentrations ranging from 0 to 50 at% (Figure 3). The second was prepared from solutions containing 30 at% fluoride and silicon amounts ranging from 1 to 5 at% (Figure S4-2). All samples analysed by XPS in this study were deposited from precursor solutions prepared in plastic labware.

The elemental analysis of the *as deposited* surfaces shows similar trends to those measured from the interior of the films. However, given the unavoidable presence of adventitious carbon on the un-etched ZnO surface, the XPS results are more likely to be quantitative for measurements on etched samples.

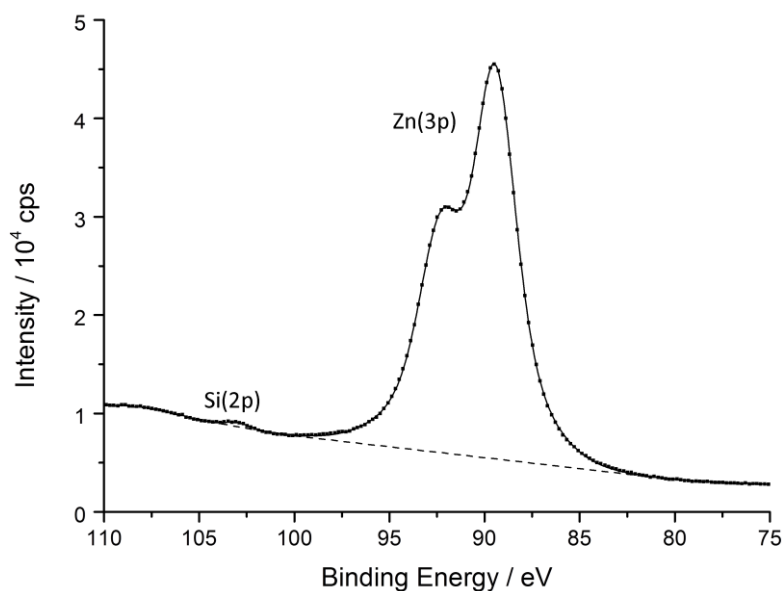


Figure S4-1 Representative XPS spectrum of a SiZO film in this study. The experimental data in a region containing Si(2p) and Zn(3p) signals for a sample prepared from a precursor solution containing 3 at% silicon and 30 at% fluoride is shown (square symbols), as are the fits to the data (solid line) and the linear backgrounds (dashed line) used to integrate each peak.

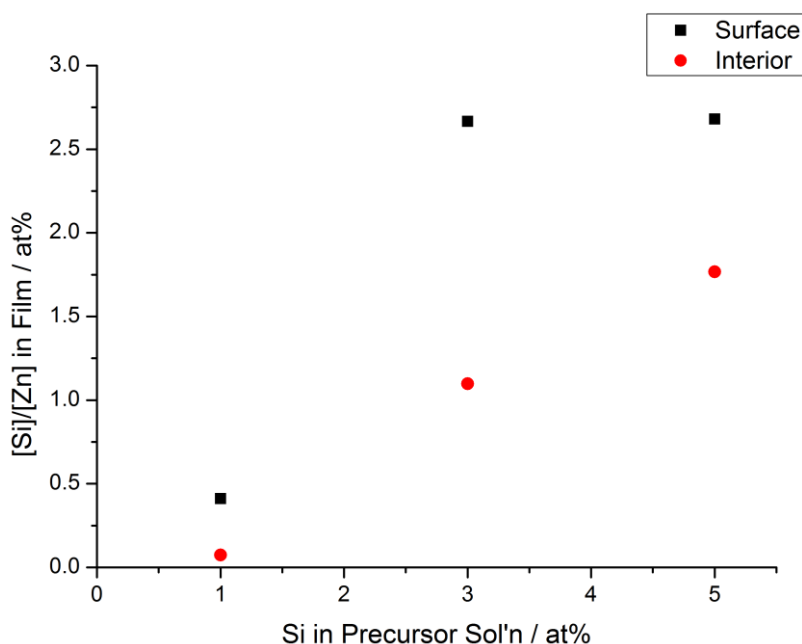


Figure S4-2 Si-to-Zn ratios at the surface (black squares) and in the interior (red circles) of SiZO thin films prepared from precursor solutions with 30 at% fluoride and varying concentrations of silicon. The ratios are calculated from the relative areas of the Si(2p) and Zn(3p) peaks.

To determine whether fluorine has been substantially incorporated into the films prepared using these deposition conditions, the XPS spectra of samples prepared with 0% and 50% F⁻ (with constant 3 at% Si) in the precursor solutions were compared near binding energies of 29.2 eV, 685.7 eV, and 833.0 eV, which are the expected locations of the F(2s), F(1s), and F-KLL Auger signals, respectively.⁸ A distinct fluorine signal was not observed at any of these locations in measurements made on either etched (Figure S4-3) or *as deposited* surfaces (Figure S4-4) of the SiZO films.

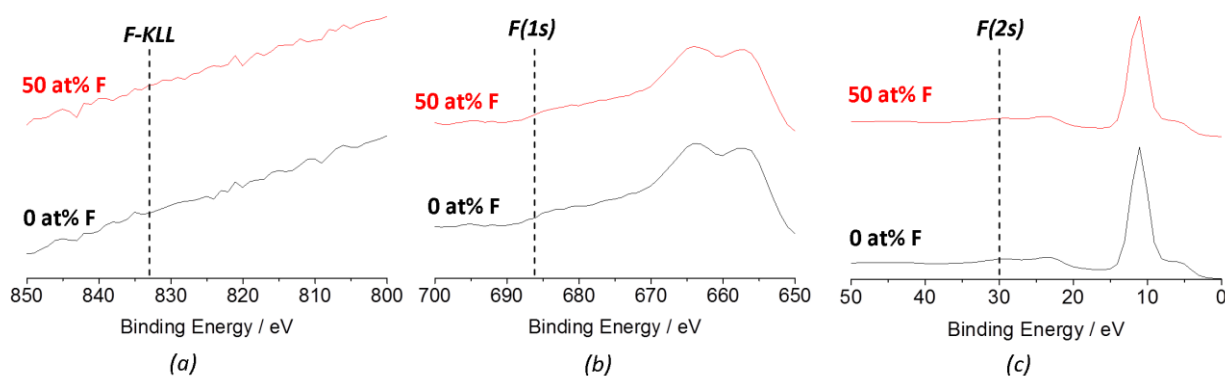


Figure S4-3 Comparison of XPS spectra of argon-etched SiZO films prepared by spray pyrolysis using precursor solutions containing 50 at% F⁻ and 3 at% Si (red lines) or 0 at% F⁻ and 3 at% Si (black lines) in 3 regions which would contain signals for fluorine if the element were present: a) F-KLL Auger, b) F(1s), and c) F(2s).

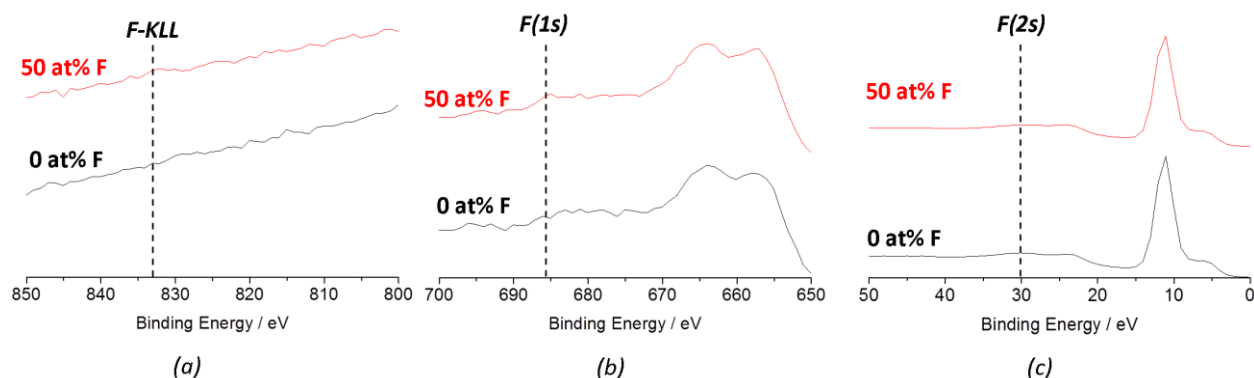


Figure S4-4 Comparison of XPS spectra of *as deposited* surfaces of SiZO films prepared by spray pyrolysis using precursor solutions containing 50 at% F⁻ and 3 at% Si (red lines) or 0 at% F⁻ and 3 at% Si (black lines) in 3 regions which would contain signals for fluorine if the element were present: a) F-KLL Auger, b) F(1s), and c) F(2s).

V. Scanning Electron Microscopy

The surface morphology of the thin films was characterised using a JEOL JSM-840F field emission scanning electron microscope at an accelerating voltage of 5 kV and using a secondary electron detector. Samples were sputter coated with a ~2 nm layer of platinum before observation to reduce the effect of surface charging and attendant artefacts.

A change in surface morphology is clearly visible as the amount of fluoride in the precursor solution is increased, even as the concentration of silicon is held constant (Figure S5-1).

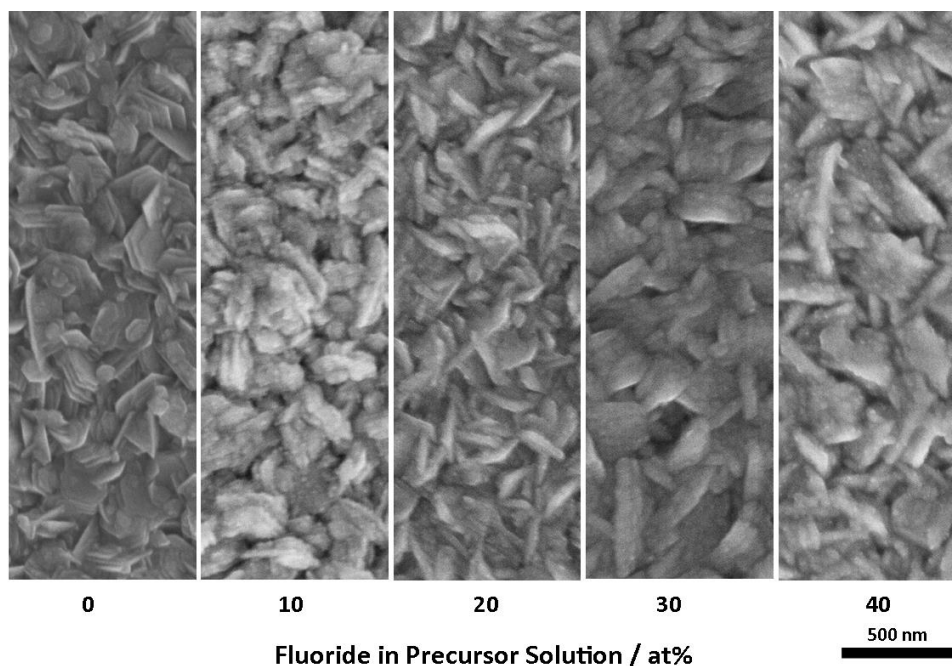


Figure S5-1 SEM data illustrating the morphology change across a series of SiZO thin films prepared by spray pyrolysis using precursor solutions with a constant silicon content of 3 at% and fluoride content ranging from 0 to 40 at%.

In addition to imaging, an energy dispersive X-ray (EDX) spectrometer attached to a JEOL JSM-5510 SEM was used to survey the sample surfaces for the presence of fluorine, which was not found.

References

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