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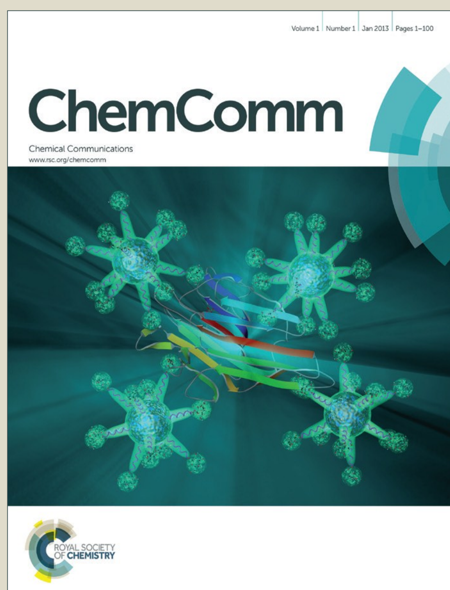

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COMMUNICATION

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

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Fluoride in spray pyrolysis precursor solutions for silicon-doped zinc oxide (SiZO) transparent conductor thin films significantly improves their electrical conductivity by enhancing silicon doping efficiency and not, as previously assumed, by fluoride doping. Containing only earth-abundant elements, SiZO thus prepared rivals the best solution-processed indium-doped ZnO in performance.

Zinc oxide (ZnO) is a prototypical *n*-type Transparent Conducting Oxide (TCO) that stands out among its peers for its high earth abundance and low toxicity.[1,2] Doped ZnO thin films prepared using solution-based techniques like spray pyrolysis,[3] which are similarly low cost and highly scalable, have already been demonstrated with electrical conductivities and optical transparencies suitable for use in a range of technologies, including touchscreen sensors, smart windows, and low-emissivity glass.[4] However, applications demanding higher electrical conductivities presently remain inaccessible to solution-processed, doped ZnO systems. For these applications, the high conductivity of doped indium oxides (most notably ITO) makes them the undisputed incumbents, despite their being several orders of magnitude costlier than ZnO.[5,6] As such, one of the longstanding challenges in this field has been to improve the performance of indium-free or reduced indium TCO materials to broaden their usefulness to higher-performance applications.

We have previously reported that silicon acts as an *n*-type donor in ZnO thin films deposited by spray pyrolysis.[7] Among the many possible dopant elements for ZnO, silicon is attractive because its use is in adherence to the principle of using low-cost, abundant materials that motivates much of the research and interest in ZnO itself. In a simple view of this doping process, the constraint of charge neutrality requires that 2 extra electrons be present for each substitution of Si^{4+} for Zn^{2+}. These dopant-derived electrons are then easily ionized from the defect site to become free carriers and therefore contribute to enhanced electronic conduction. At a 4 at% silicon doping level, an average sheet resistance of 82 Ω/□ and an average visible transparency of 89% (corrected for glass substrate) are observed for SiZO samples of ~580 nm thickness, corresponding to an electrical conductivity of ~210 Ω^{-1} cm^{-1}.

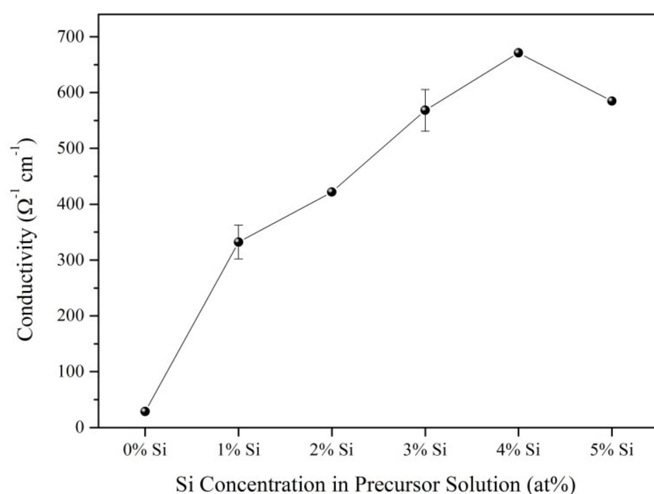

Figure 1: Electrical conductivity of ZnO and SiZO films prepared from precursor solutions containing 30 at% fluoride and varying amounts of silicon.

Now, we have observed that addition of fluoride to SiZO spray pyrolysis precursor solutions results in a significant improvement in electrical conductivity. For example, when a precursor solution containing 30 at% fluoride (as ammonium fluoride) and 4 at% silicon (as silicon tetraacetate) is decomposed at a substrate surface temperature of 376 °C, the resulting thin film exhibits an electrical conductivity of ~670 Ω^{-1} cm^{-1} and a transparency of 87% without any post-deposition treatment (Figure 1). For a sample thickness determined as 520 nm, this corresponds to a sheet resistance of ~29 Ω/□. The electrical performance for this entirely indium-free system is comparable to the best reliably reported values for doped ZnO thin films prepared by spray pyrolysis ($\sigma \approx 770$ Ω^{-1} cm^{-1}), which have been achieved only by using costly indium as a dopant, and, in one case, only after post-depositional annealing in vacuum.[4,8]

Interestingly, the combination of Si and F in the precursor solutions produces results that apparently cannot be achieved by using either element alone (Figure 2). While there is ample literature

on co- or multiply-doped ZnO, some reports are aimed at preparing *p*-type ZnO through the use of mutually compensating dopants.[9,10] Where the goal has been highly conducting *n*-type films, ZnO with both cation-cation and cation-anion doping systems have been proposed and reportedly prepared using a wide range of deposition techniques.[11-18] However, we are not aware of any case where the two additives chosen show a clear synergistic effect, that is, where the effect of the combination is greater than the sum of the individual contributions.

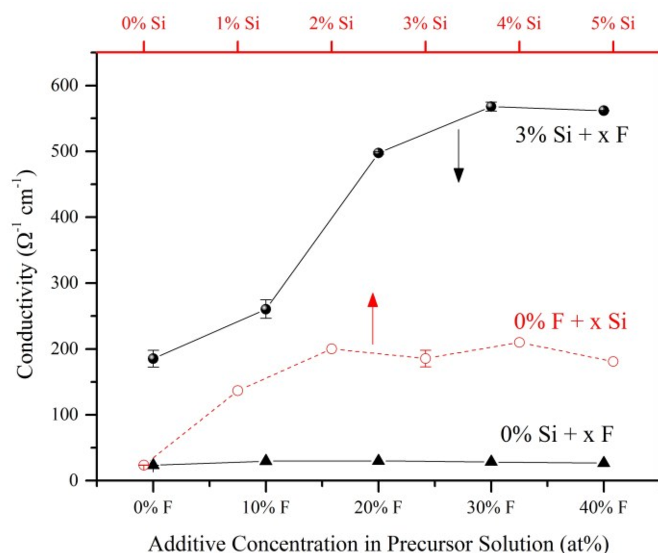

Figure 2: Electrical conductivity of various ZnO and SiZO films prepared from precursor solutions with a variety of silicon and fluoride concentrations. Data are presented in 3 series: fluoride only (black triangles), silicon only (red circles), and varying fluoride at 3 at% silicon concentration (black circles).

Fluoride would be expected to act as an *n*-type dopant if it substituted for oxide in the ZnO lattice. Indeed, where vacuum-based techniques have been used to deposit fluorine-doped ZnO, a link between fluorine incorporation and enhanced electrical conductivity can generally be demonstrated.[18-20] The situation is more complex with films deposited by spray pyrolysis, where conductivity enhancement attributed to fluorine doping has also previously been reported.[21-23] However, our results appear to contradict this by showing that the addition of *only* fluoride to the spray pyrolysis precursor solution does not appreciably alter the electrical properties of resulting ZnO films if the solutions are consistently handled in plastic laboratory ware. Only by using glassware have we been able to reproduce enhanced electrical conductivity in “fluorine-doped” ZnO deposited by spray pyrolysis (ESI §2). On the basis of ^{19}F NMR experiments on fluoride-containing precursor solutions handled in glassware (ESI §3), we propose that the reported improvements occurred because of unintentional doping by glass components extracted into the precursor solution by interaction with the aqueous fluoride ion (of which silicon, importantly, is likely to be a significant part). Even if some effect could have been attributed to substitutional doping of fluorine, the $\sim 3 \times 10^{20}$ cm^{-3} increase in carrier concentration upon going from 0 to 30 at% F^- (at constant 3 at% Si) in the precursor solutions is much too large to be accounted for by simple addition of the individual silicon and fluorine contributions (Figure 3).

Because the elemental composition of a deposited film can, in general, differ quite dramatically from that of the precursor solution,

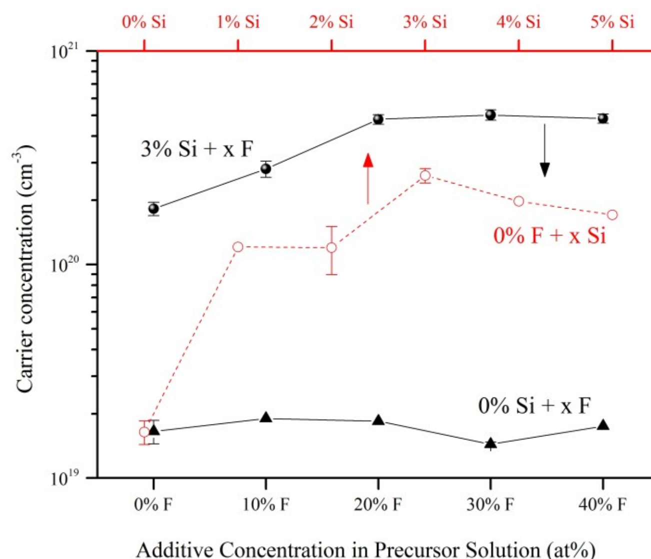

Figure 3: Carrier concentrations in various ZnO and SiZO films prepared from precursor solutions containing varying amounts of silicon and fluoride. Data are presented in 3 series: fluoride only (black triangles), silicon only (red circles), and varying fluoride at 3 at% silicon concentration (black circles).

the actual silicon-zinc ratio in the thin films was determined by comparison of the relative integrals of the Si(2p) and Zn(3p) signals in the X-ray photoelectron spectroscopy (XPS) spectrum. Samples were etched with argon plasma prior to analysis to minimise the influence of surface contamination and to provide the clearest measurement of bulk sample composition. Using precursor solutions with a fixed silicon concentration, increasing the concentration of fluoride led to a monotonic increase in silicon incorporation into the films up to at least 50 at% F^- (Figure 4). The greater amount of silicon in the films is the most straightforward explanation for increased carrier concentration, and hence electrical conductivity. Nevertheless, it should be noted that the relative increase in silicon content is larger than the corresponding increase in carrier concentration, suggesting that some of the silicon in the films is present in an electrically inactive form.

As further evidence that fluorine is not contributing significantly to electrical conductivity as a dopant, we have also found using this XPS data, as well as energy-dispersive X-ray (EDX) spectroscopy, that the concentration of fluorine is below detection limits in all samples (Figure 4, ESI §4).

Instead of acting as a dopant in its own right, the fluoride acts by modifying the solution behaviour of silicon-containing species in a way that increases the amount of electrically-active silicon eventually incorporated into the ZnO lattice. In aqueous solutions, dissolved silicon in the form of silicic acid—$Si(OH)_4$—is known to participate in condensation reactions, which lead to the formation of various oligomers, colloidal silica, or even an extended-network solid gel, depending on the conditions. Solution equilibria favour condensation reactions when the silicon concentration is high and the pH is slightly acidic, both of which are true for the precursor solutions used here.[24,25] Based on the observation that commercially-available suspensions of colloidal silica (such as Ludox®) are not effective silicon sources for the preparation of SiZO by spray pyrolysis, it appears that silicon most effectively dopes into the growing ZnO lattice when present in solution as monomeric or small oligomeric species. Perhaps analogous is the case in the classic colorimetric analysis for dissolved silica, where the silicon in

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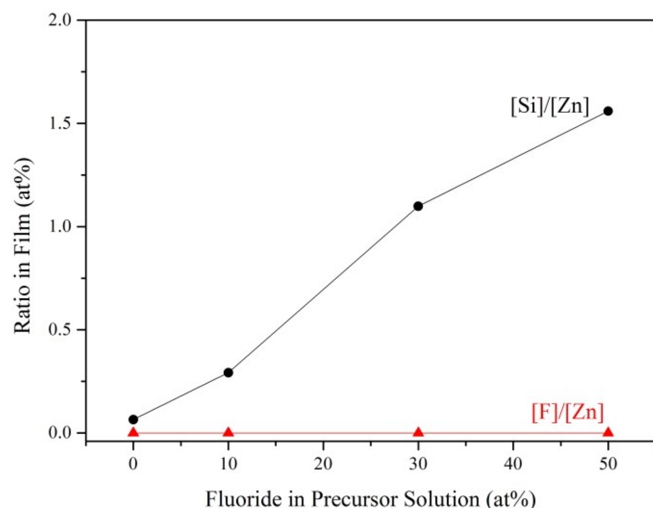

Figure 4: Si-to-Zn (black circles) and F-to-Zn (red triangles) ratios in the interior of SiZO thin films prepared from precursor solutions with a fixed 3 at% Si concentration and varying amounts of fluoride. The Si-to-Zn ratio is calculated from the areas of the Si(2p) and Zn(3p) XPS peaks recorded after argon plasma etching of the sample surface. Fluorine is below detection limits in all samples.

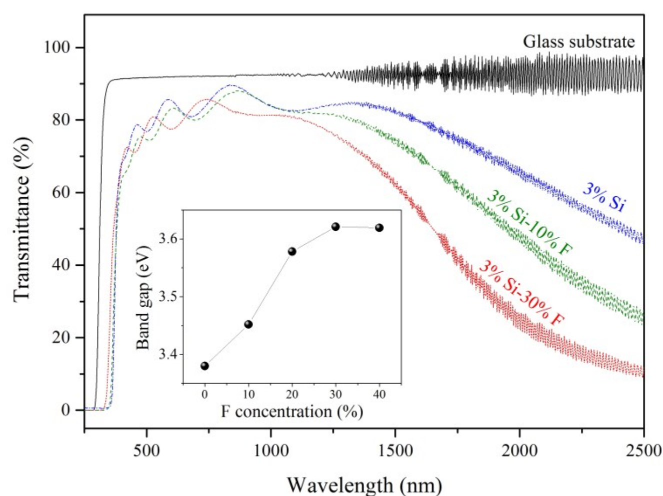

Figure 5: UV-Vis-NIR optical transmission spectra of SiZO thin films prepared from precursor solutions containing 3 at% Si and varying amounts of fluoride. The increasing carrier concentration with fluoride addition manifests both as a blueshift of the plasma edge in the near-IR and as a widening of the optical band gap as calculated from the Tauc relation (inset). The transmission spectrum of a bare glass substrate is provided for reference.

polymerised forms of silica does not readily incorporate into the yellow-coloured silico-12-molybdic acid upon reaction with ammonium heptamolybdate.[26]

To confirm this hypothesis, solutions containing various ratios of silicon tetraacetate to ammonium fluoride in a model solvent designed to mimic that used for the spray pyrolysis precursor solutions were prepared in plastic labware and examined by ^{19}F NMR (additional details in ESI §3). For each sample, an NMR signal with a variable chemical shift was observed, which we assign to fluoride participating in a pH dependent F^-/HF equilibrium.[27] Whenever silicon (whether extracted from glass or added as silicon tetraacetate) and fluoride are both present, rapid development of a sharp signal at $\delta \approx -129.1$ ppm can be ascribed to formation of the SiF_6^{2-} anion that occurs in equilibrium with "unbound" fluoride. This observed value falls into the reported chemical shift range for the aqueous SiF_6^{2-} ion of −130.5 to −128.2 ppm and also matches the signal observed when zinc hexafluorosilicate is dissolved in the same solvent.[28] These observations are clearly consistent with a substantial silicon-fluorine interaction in solution. The presence of relatively stable SiF_6^{2-} would reduce the effective concentration of silicon oxy and hyrdoxy species available for self-condensation reactions and leave a larger proportion of silicon available in a monomeric, doping-active form.

This model allows ready interpretation of the optical and electrical properties of SiZO thin films prepared using fluoride-containing precursor solutions. Hall effect measurements (Figure 3) confirm that improved electrical conductivity with fluoride addition stems from a substantial increase in carrier concentration, while carrier mobility is not significantly affected. In the UV-Vis-NIR transmission spectra of films made from solutions with constant silicon and variable fluoride concentrations, both a Burstein-Moss widening of the optical bandgap (as calculated using the Tauc relation) and an increase in near-infrared reflectivity occurs with increasing fluoride content (Figure 5).[29-31] Both phenomena are consistent with the increasing concentration of free carriers that arises from enhanced silicon incorporation into the ZnO lattice.

All samples studied here give XRD patterns consistent with ZnO in the hexagonal wurtzite structure. No other crystalline phases were observed. As is typical for most thin film ZnO samples prepared by spray pyrolysis, the intensity distribution of the XRD peaks indicates that the crystallites in the films have grown with a preferred orientation relative to the substrate. We find that an increasing fluoride concentration in the precursor solution leads to a change in crystallite orientation from (002) and (101) oriented to a configuration more closely resembling random orientation (Figure 6), possibly corresponding with changes in surface morphology visible in SEM images (ESI §5). It is well known that increased dopant content can alter the direction and extent of preferred orientation for crystallites in ZnO thin films.[7,32,33] Accordingly, these structural changes in SiZO can be rationalized by considering the increased amount of silicon in the films due to the action of fluoride in the precursor solution.

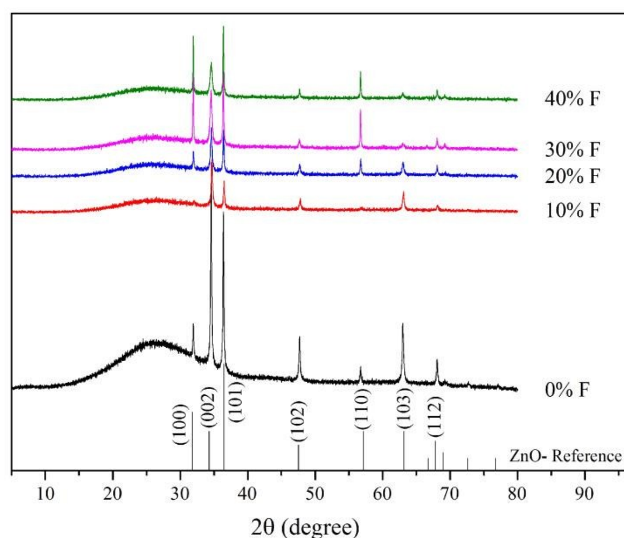

Figure 6: X-ray diffraction patterns of SiZO films prepared from precursor solutions containing 3 at% Si, showing changes in preferred orientation upon varying the amount of fluoride. All patterns are consistent with ZnO in the wurtzite structure (reference stick chart at bottom).

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Conclusions

A substantial improvement in the electrical conductivity of SiZO thin films deposited by spray pyrolysis occurs when fluoride is added to the precursor solutions. This results in an indium-free TCO that rivals the best doped ZnO materials (including indium-doped zinc oxides) yet produced by this deposition technique. Chemical analysis of the resulting films indicates that the mechanism is not the co-doping of Si and F as has previously been suggested, but rather a fluoride-enhanced incorporation of Si into the ZnO thin film.

Silicon and fluorine may not be the only combination of elements that will show such a synergistic effect when used in the solution preparation of ZnO. For example, another potentially interesting combination may be fluorine and aluminium, which like silicon and fluorine share the characteristics of strong mutual interaction and potential as an earth-abundant dopant system for ZnO. Hopefully, this communication demonstrates the importance of examining precursor solution chemistry while attempting to tune the optoelectronic properties of TCO thin films deposited by solution routes, and inspires further work on this heretofore understudied approach to improving the performance of low cost, earth-abundant TCO materials.

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Notes and references

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1 C. W. Litton, D. C. Reynolds and T. C. Collins, *Zinc Oxide Materials for Electronic and Optoelectronic Device Applications*, Wiley, Chichester, UK, 2011.

2 Z. C. Feng, *Handbook of Zinc Oxide and Related Materials*, CRC Press, Boca Raton, FL, 2012.

3 J. B. Mooney and S. B. Radding, *Ann. Rev. Mater. Sci.,* 1982, **12**, 81-101.

4 S. Major, A. Banerjee and K. L. Chopra, *J. Mater. Res.,* 1986, **1**, 300-310.

5 D. Ginley, H. Hosono and D. C. Paine, *Handbook of Transparent Conductors*, Springer, New York, 2011.

6 K. Ghaffarzadeh and R. Das, *Transparent Conductive Films (TCF) 2013-2023: Forecasts, Technologies, and Players*, IdTechEx, Cambridge, UK, 2013.

7 N. Rashidi, V. L. Kuznetsov, J. R. Dilworth, M. Pepper, P. J. Dobson and P. P. Edwards, *J. Mater. Chem. C,* 2013, **1**, 6960-6969.

8 R. Biswal, L. Castañeda, R. Moctezuma, J. Vega-Pérez, de la L. Olvera, M. and A. Maldonado, *Materials,* 2012, **5**, 432-442.

9 T. Yamamoto, *physica status solidi (a),* 2002, **193**, 423-433.

10 M. Joseph, H. Tabata and T. Kawai, *Jap. J. Appl. Phys.,* 1999, **38**, L1205-L1207.

11 J. Kim, J. Bae, T. Hong, M. Won, J. Yoon, B. Lee and H. Lee, *Thin Solid Films,* 2010, **518**, 6179-6183.

12 J. Nomoto, T. Miyata and T. Minami, *J. Vac. Sci. Technol., A,* 2009, **27**, 1001-1005.

13 D. C. Altamirano-Juárez, G. Torres-Delgado, S. Jiménez-Sandoval, O. Jiménez-Sandoval and R. Castanedo-Pérez, *Sol. Energy Mater. Sol. Cells,* 2004, **82**, 35-43.

14 B. G. Choi, I. H. Kim, D. H. Kim, K. S. Lee, T. S. Lee, B. Cheong, Y. -. Baik and W. M. Kim, *J. Eur. Ceram. Soc.,* 2005, **25**, 2161-2165.

15 T. V. Vimalkumar, N. Poornima, K. B. Jinesh, C. S. Kartha and K. P. Vijayakumar, *Appl. Surf. Sci.,* 2011, **257**, 8334-8340.

16 A. Maldonado, J. Rodríguez-Baez and M. de la L. Olvera, *Mater. Chem. Phys.,* 2011, **129**, 109-115.

17 E. F. Keskenler, G. Turgut and S. Doğan, *Superlattices Microstruct.,* 2012, **52**, 107-115.

18 Y. Thimont, J. Clatot, M. Nistor, C. Labrugère and A. Rougier, *Sol. Energy Mater. Sol. Cells,* 2012, **107**, 136-141.

19 H. S. Yoon, K. S. Lee, T. S. Lee, B. Cheong, D. K. Choi, D. H. Kim and W. M. Kim, *Sol. Energy Mater. Sol. Cells,* 2008, **92**, 1366-1372.

20 X. Noirfalise, T. Godfroid, G. Guisbiers and R. Snyders, *Acta Mater.,* 2011, **59**, 7521-7529.

21 M. de la L. Olvera, A. Maldonado, R. Asomoza, O. Solorza and D. R. Acosta, *Thin Solid Films,* 2001, **394**, 241-248.

22 A. Maldonado, R. Asomoza, J. Cañetas-Ortega, E. P. Zironi, R. Hernández, R. Patiño and O. Solorza-Feria, *Sol. Energy Mater. Sol. Cells,* 1999, **57**, 331-344.

23 R. R. Biswal, S. Velumani, B. J. Babu, A. Maldonado, S. Tirado-Guerra, L. Castañeda and M. de la L. Olvera, *Mater. Sci. Eng. B-Adv.,* 2010, **174**, 46-49.

24 O. Weres, A. Yee and L. Tsao, *J. Colloid Interface Sci.,* 1981, **84**, 379-402.

25 S. H. Chan, *Geothermics,* 1989, **18**, 49-56.

26 T. Coradin, D. Eglin and J. Livage, *Spectroscopy,* 2004, **18**, 567-576.

27 J. B. Gerken, *J. Fluorine Chem.,* 2011, **132**, 68-70.

28 W. F. Finney, E. Wilson, A. Callender, M. D. Morris and L. W. Beck, *Environ. Sci. Technol.,* 2006, **40**, 2572-2577.

29 E. Burstein, *Phys. Rev.,* 1954, **93**, 632-633.

30 T. S. Moss, *Proc. Phys. Soc., London, Sect. B,* 1954, **67**, 775-782.

31 J. Tauc, R. Grigorovici and A. Vancu, *physica status solidi (b),* 1966, **15**, 627-637.

32 D. J. Goyal, C. Agashe, M. G. Takwale, V. G. Bhide, S. Mahamuni and S. K. Kulkarni, *J. Mater. Res.,* 1993, **8**, 1052-1056.

33 P. Nunes, E. Fortunato, P. Tonello, F. Braz Fernandes, P. Vilarinho and R. Martins, *Vacuum,* 2002, **64**, 281-285.

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