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LETTER TO THE EDITOR

Evidence for SiF_6^{2-} ions in electrochemically deposited Si:O:F films and plasma-enhanced chemically vapour deposited Si:O:H:F alloys

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Abstract. Using infrared absorption spectroscopy data from electrochemically deposited Si:O:F films and plasma-enhanced chemically vapour deposited Si:O:H:F alloys we report the presence of SiF_6^{2-} ions within both fluorine-doped silicon oxide thin films.

The study of fluorine bonding in fluorine-doped silicon oxide materials has aroused much interest regarding the development of optical fibres (Rabinovich 1983) and novel low-temperature ($\leq 600^\circ\text{C}$) grown dielectric materials (Morita *et al* 1985, 1986). In this Letter we use infrared absorption spectroscopy (IR) to emphasise the presence of SiF_6^{2-} ions in electrochemically deposited (ED) and plasma-enhanced chemically vapour deposited (PECVD) fluorine-doped silicon oxide thin films.

The ED Si:O:F films were produced by cathodic deposition of solutions of tetrabutylammonium hexafluorosilicate ($(\text{TBA})_2\text{SiF}_6$) in dimethylsulphoxide (DMSO) (Pimenta *et al* 1988). The PECVD Si:O:H:F alloys were deposited by radiofrequency glow discharge of $\text{SiH}_4/\text{F}_2/\text{Ar}$ gas mixtures (Dias *et al* 1988b). The IR absorption spectra of both films were recorded using a Perkin–Elmer 683 double-beam spectrophotometer operated in the transmittance mode. The oxygen incorporation in ED Si:O:F films resulted from electrolyte dissociation, whereas that in PECVD Si:O:H:F was traced down to residual oxygen and oxygenated compounds from the fluorine container and to the etching of the Pyrex wall of the reactor chamber by fluorine-active species (Dias *et al* 1988a).

Figure 1(a) shows the region between 900 cm^{-1} and 400 cm^{-1} of the IR spectra of an ED Si:O:F film deposited at constant potential (-2.900 V) onto crystalline silicon (c-Si), recorded compensating the absorption in the c-Si substrate with a clean substrate placed in the reference beam. The same spectral range of the IR spectra of a pressed KBr disc 1 mm thick containing powdered $(\text{TBA})_2\text{SiF}_6$ is also shown in figure 1(b). The vibrational structure with maximum at 720 cm^{-1} and the band centred at 480 cm^{-1} , previously reported in cathodic-deposited silicon films produced in solutions of K_2SiF_6 in acetone and HF and of SiF_4 in acetonitrile, has been associated (Lee and Kroger 1982) with poly-fluorinated compounds. Nevertheless, the similarity of these vibrational

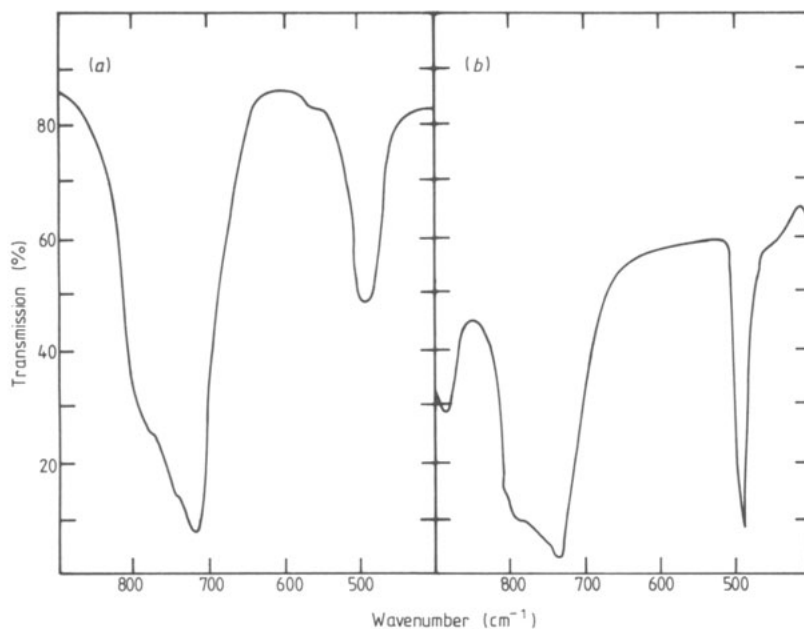


Figure 1. Infrared absorption spectra of (a) an electrochemically deposited Si:O:F film 2.5 μm thick and (b) a pressed KBr disc with powdered $(\text{TBA})_2\text{SiF}_6$.

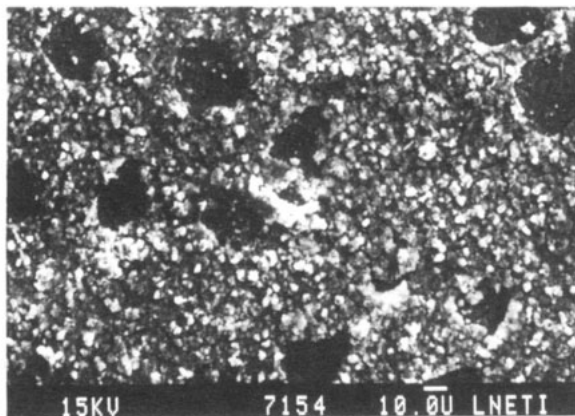


Figure 2. SEM micrograph of the electrochemically deposited Si:O:F film of figure 1(a) after annealing at 300 $^{\circ}\text{C}$.

modes to the ones from the hexafluorosilicate ions of the $(\text{TBA})_2\text{SiF}_6$ solute, also shown in figure 1(b), suggests the assignment of the 720 cm^{-1} and 480 cm^{-1} bands respectively to the stretching and bending vibrations of SiF_6^{2-} ions (Badachhape *et al* 1966) from $(\text{TBA})_2\text{SiF}_6$ occluded in our ED Si:O:F films. The formation of large holes on the surface of these films upon annealing, as shown in figure 2, is a result of the thermal evolution of electrolyte ($(\text{TBA})_2\text{SiF}_6$ solved in DMSO) inclusions, providing further evidence for the above assignments.

Figure 3 shows the region between 800 cm^{-1} and 400 cm^{-1} of the IR spectra of a PECVD Si:O:H:F alloy deposited at low substrate temperature (100 $^{\circ}\text{C}$) in the same run

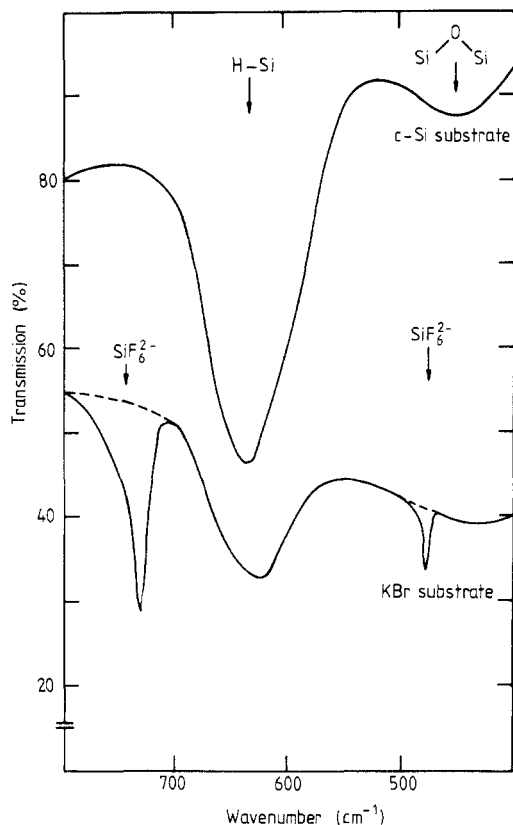


Figure 3. Infrared absorption spectra of a plasma-enhanced chemically vapour deposited Si:O:H:F alloy, 3.2 μm thick, simultaneously deposited onto c-Si and KBr substrates.

respectively onto c-Si and KBr substrates. In the IR spectra of the film deposited onto c-Si the absorption from the substrate was compensated using the procedures previously described for ED Si:O:F films. Uncompensated IR spectra of films deposited on KBr monocrystals 1.5 mm thick with high transmittance ($\approx 85\%$) were also recorded. The absorptions located at 630 cm^{-1} and 450 cm^{-1} are respectively the wagging vibrations of Si-H bonds and the rocking oxygen motions in OSiO_3 complexes. The rather strong absorption centred at 730 cm^{-1} and the sharp band at 480 cm^{-1} are a result of the IR activity of SiF_6^{2-} anions with octahedral symmetry constituted in the presence of the low-electronegativity cations from the KBr substrates (Badachhape *et al* 1966). These bands, not seen in the IR spectra of the Si:O:H:F film deposited onto c-Si, shift to lower frequencies in films deposited onto NaCl substrates, according to previous vibrational studies of hexafluorosilicates of potassium and sodium (Badachhape *et al* 1966, Sharp and Coyle 1972).

In conclusion, we have provided spectroscopic evidence for the presence of SiF_6^{2-} ions in electrochemically deposited Si:O:F and plasma-enhanced chemically vapour deposited Si:O:H:F alloys. These ions are associated respectively with tetrabutylammonium hexafluorosilicate occlusions of the electrolyte or with hexafluorosilicates of potassium (sodium) formed in films deposited onto potassium bromide (sodium chloride) substrates.

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References

- Badachhpe R B, Hunter G, McCory L D and Margrave J L 1966 *J. Inorg. Chem.* **5** 926
- Dias A G, Bustarred E and Silva R C 1988a *The Physics and Technology of Amorphous Silica* ed. R Devine (New York: Plenum) p 353
- Dias A G, Guimarães L and Brunel M 1988b *The Physics and Technology of Amorphous Silica* ed. R Devine (New York: Plenum) p 359
- Lee C H and Kroger F A 1982 *J. Electrochem. Soc.* **129** 936
- Morita M, Aritome S, Tanaka T and Hirose M 1986 *Appl. Phys. Lett.* **49** 699
- Morita M, Aritome S, Tsukude M, Murakawa T and Hirose M 1985 *Appl. Phys. Lett.* **47** 253
- Pimenta G, Gama V and Almeida M 1988 *Proc. Nato ASI Spectroscopic and Diffraction Techniques in Interfacial Electrochemistry (Puerto de la Cruz, Spain)* unpublished
- Rabinovich E M 1983 *Phys. Chem. Glass.* **24** 54
- Sharp K G and Coyle T D 1972 *J. Inorg. Chem.* **11** 1259