DOI: 10.1017/S1431927605501090
Microsc Microanal 11(Suppl 2), 2005
Copyright 2005 Microscopy Society of America

THE USE OF EELS TO STUDY THE URBACH EDGE OF SILICA

S. C. Cheng, S. L. Schiefelbein, L. Moore, M. Pierson-Stull, S. Sen and C. Smith

Science and Technology, Corning Incorporated, Corning, NY 14831

Silica, with its large band gap (~8 eV) and high transmission in the ultraviolet, is the material of choice for optical components in photolithography systems employing KrF (248 nm, 5.0 eV) and ArF (193 nm, 6.4 eV) lasers. Improved transmission is desired to improve efficiency and extend the range of usable laser wavelengths (*e.g.* to F_2 lasers which operate at 157 nm, 7.9 eV). It is well known that impurities influence transmission, and there is some evidence that transmission is influenced by structure [1], and that structure affects the Urbach edge [2]. In order to better understand the influence of structure, we undertook to study the relationships between the Urbach edge, transmission at 193 nm (%T_i @193 nm) and fictive temperature (T_f), which is thought to be a measure of glass structure.

The Urbach edge is typically studied via measurements of the optical absorption coefficient (α). However, since absorption increases with energy, direct measurement of α above ~8 eV is very difficult, and a new method was needed to investigate the Urbach edge of silica. In this study, α in the energy range 0-40 eV was obtained from low loss EELS data by Kramers-Kronig analysis [3]. The EELS experiments were carried out using a 200 kV cold field emission TEM (Hitachi HF-2000) equipped with a Gatan 666 parallel EELS spectrometer interfaced via the Gatan EL/P software to a PC. The microscope was set in image mode and no objective lens aperture was used (energy resolution ~0.6 eV). Prior to the EELS experiment, specimens were examined on the JEM-2000FX microscope equipped with an Evex ultra-thin window X-ray detector.

Figure 1 is a raw EELS spectrum over the range 0-40eV taken from a silica sample. After removing the contributions of multiple scattering, a single scattering profile was obtained and is shown in Fig. 2. Next, the surface scattering contribution was removed and the Kramers-Kronig analysis was applied to yield α as a function of energy, as shown in Fig. 3. The band gap energy (E_0) can be estimated from the plot at the point, near 10 eV, where the slope changes abruptly. Because α of silica glasses can be expressed as an exponential function of energy E [4], the slope of the Urbach edge, K, can be determined from the slope of the straight line in the graph of $ln(\alpha)$ *vs.* E, shown in Fig. 4. Applying this analysis to several groups of silica samples, it was found that E_0 varied very little (less than 5%), and no obvious relationship was observed between E_0 and %T_i @193 nm. However, K appeared to be related to %T_i @193 nm. As shown in Fig. 5, the samples with higher K have higher %T_i@193 nm. In order to investigate the relationship between T_f and K, four samples of F-doped silica with different T_f were studied. The different T_f were achieved by specific heat treatments and were measured by FT-IR transmission spectroscopy. The results suggest a relationship between K and T_f. As shown in Fig. 6, the samples with lower T_f have higher K.

In summary, EELS was successfully applied to the study of the Urbach edge of silica. The results support the idea that structure affects transmission, and suggest that transmission can be improved by achieving a more relaxed glass structure.

Acknowledgements
The authors gratefully acknowledge Drs. J.G. Zheng, S.Y. Li and V.P. Dravid for the use of their

https://doi.org/10.1017/S1431927605501090 Published online by Cambridge University Press

facilities at EPIC of Northwestern University.

References
1. H. Hosono, Y. Ikuta, T. Kinoshita, and M. Hirano, Phys. Rev. Lett. **87** (2001) 175501.
2. K. Saito and J. Ikushima, J. Appl. Phys. **91** (2002) 4886.
3. R. F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope*, 2nd edition, Plenum Press, New York, (1996).
4. I. T. Godmanis, A. N. Trukhin, and K. Hubner, Phys. Stat. Sol. (b) **116** (1983) 279.

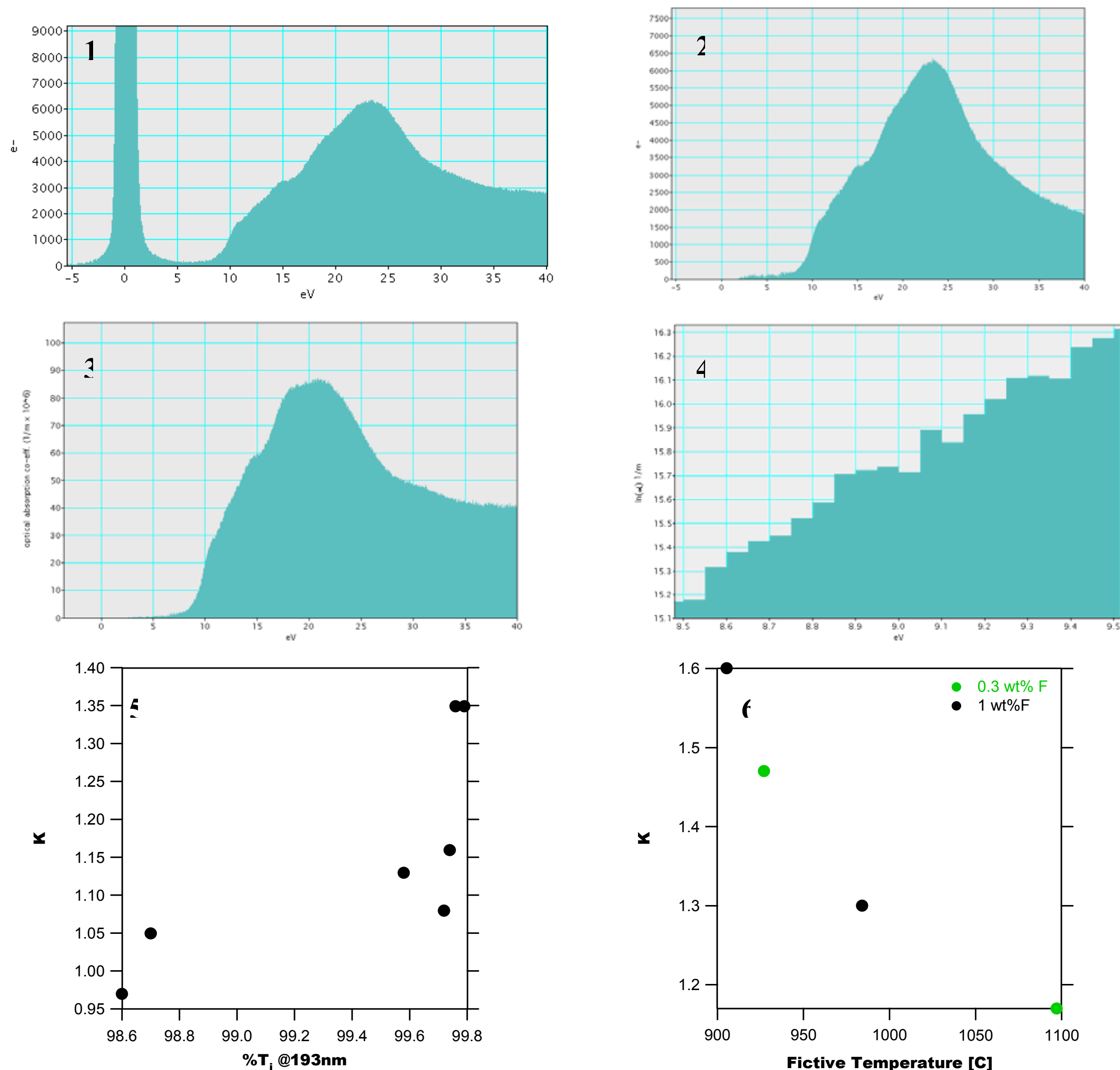

Fig. 1. A raw EELS spectrum taken from an example silica specimen.
Fig. 2. The single scattering profile obtained after Fourier-log deconvolution of the raw data.
Fig. 3. The optical absorption coefficient as a function of energy.
Fig. 4. The linear relationship between ln(α) and E at energy range from 8.5 eV to 9.5 eV.
Fig. 5. The correlation between the slope of the Urbach edge, K, and transmission @193nm.
Fig. 6. The correlation between the slope of the Urbach edge, K, and fictive temperature, T_f, for the four F-doped silica samples.