

MEASUREMENT OF THE THICKNESS OF ORGANIC THIN FILMS BY APPLYING THE BETHE SUM RULE TO ELECTRON ENERGY-LOSS SPECTRA

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Organic thin-film devices are rapidly developing and a routine method of measuring the thickness of an organic film is desirable, particularly if this enables the measurement of local thickness with good spatial resolution. Techniques that employ a transmission electron microscope (TEM) are attractive, since the spatial resolution can then be as small as 1 nm. Electron energy-loss spectroscopy (EELS) in the TEM has been utilised, but usually requires knowledge of the inelastic mean free path (MFP) for scattering in the material whose thickness is being measured [1,2]. Here we show the feasibility of using TEM/EELS to measure local thickness of organic films (containing mostly C and H) without knowledge of the MFP. The method is based on the Bethe (oscillator-strength) sum rule.

According to the Bethe sum rule [3,4], the mass thickness ρt of a specimen is given by:

$$\rho t = \frac{B m_n T}{4 \pi a_0^2 R^2 I_0} \int_0^\infty \frac{E \cdot S(E)}{\ln(1 + \beta^2 / \theta_E^2)} dE \quad (1)$$

where $B=A/Z$ (A = atomic weight and Z = atomic number), $m_n=1.67 \times 10^{-27}$ kg is the atomic mass unit; $\theta_E=E/2\gamma T$ ($T=m_0 v^2/2$ is a relativistically modified incident-beam energy) is the characteristic angle for inelastic scattering at energy loss E , $\gamma = 1/\sqrt{1 - v^2/c^2}$ being the usual relativistic factor for an electron whose incident velocity is v ; I_0 is the integrated intensity in zero-loss peak and $S(E)$ single-scattering intensity within the energy-loss spectrum, which can be derived by Fourier-log deconvolution [3], β is the collection semiangle used for the EELS data acquisition, $R = 13.6$ eV and $a_0 = 0.0529$ nm.

Thin organic specimens (p-terphenyl and perylene) were prepared by thermal evaporation in a vacuum $\sim 10^{-6}$ torr. Silicon wafers ($3 \times 3 \text{ cm}^2$) coated with a KCl thin film were used as the substrates. Source materials were loaded into a Mo boat with a large open area ($\sim 1 \times 2 \text{ cm}^2$). With a distance of ~ 15 cm between the source and substrate, the condensed thin film covered the silicon wafer uniformly (as indicated by the reflection fringes). The mass thickness of the organic film was directly measured by weighing the substrate before and after evaporation, and from the readings of a quartz-crystal film-thickness monitor during film deposition. The film was then floated off onto a water surface and picked up by a TEM grid for EELS measurement.

The electron energy loss spectrum was recorded in a JEOL-2010 TEM equipped with a Gatan-666 EELS spectrometer. Since Eq.(1) contains energy loss E as a weighting factor, the energy-loss spectrum must normally be recorded up to a high energy loss, requiring a relative high electron dose (which may cause damage, including mass loss) and elaborate correction for the stray-scattering in the spectrometer [4]. But for hydrocarbon specimens (where the H atoms contribute little to the scattering), integration of Eq.(1) only up to 280eV should be sufficient, since only four valence electrons (the appropriate value $Z=4$) contribute the energy loss below 280eV (the carbon K-shell ionization energy). To illustrate validity of this

simplification, Fig. 2 shows the integral: $M(E) = \int_0^E \frac{E \cdot S(E)}{\ln(1 + \beta^2 / \theta_E^2)} dE$ as a function of the upper limit of integration for a carbon film. The E-dependence seen here confirms the expected ratio ~ 1.5 between $M(\infty)$ and $M(280\text{eV})$.

To measure the thickness of our organic films, we therefore integrated $M(E)$ up to 280eV , taking $Z = 4$. Our spectrum was recorded in image mode and the collection semiangle was defined by an objective aperture. $S(E)$ and I_0 were obtained by a deconvolution routine incorporated into the Gatan software and Eq.(1) was evaluated using a simple computer algorithm. Table 1 shows the results of EELS measurement (applying our procedure to six spectra and taking an average) in comparison with the weighed thickness of each film. Agreement is within 10%, which is sufficient for many purposes.

References:

- [1] R.F. Egerton and S.C. Cheng, *Ultramicroscopy*, 21 (1987) 231-244.
- [2] Y.-Y. Yang and R.F. Egerton, *Micron*, 26 (1995) 1-5.
- [3] R.F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope*, 2nd edition (Plenum, New York, 1996).
- [4] P.A. Crozier and R.F. Egerton, *Ultramicroscopy*, 27 (1989) 9-18.

Figures:

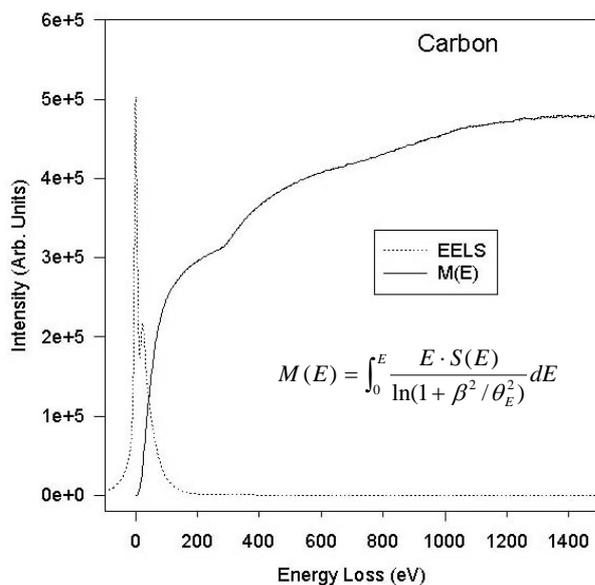


Fig.1: Energy-loss spectrum of carbon and the function $M(E)$, demonstrating the ratio of $M(\infty)/M(280) \sim 1.5$.

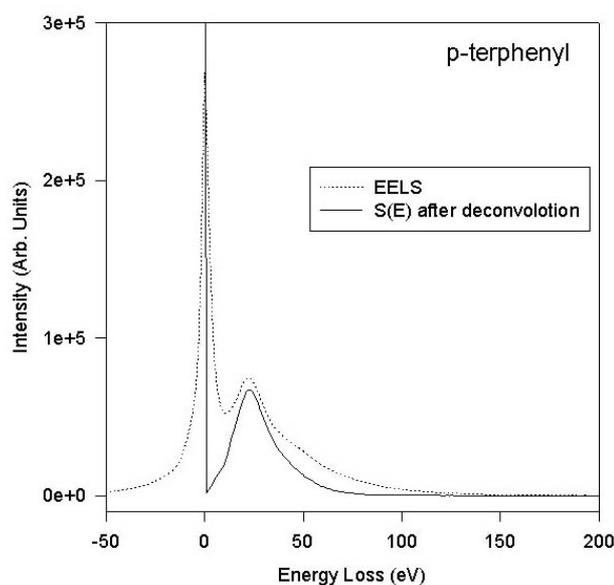


Fig.2: P-terphenyl energy-loss spectrum and its single scattering distribution $S(E)$ obtained after deconvolution by the Fourier-log method.

organic material	weighing ($\mu\text{g}/\text{cm}^2$)	thickness monitor ($\mu\text{g}/\text{cm}^2$)	EELS Bethe sum rule ($\mu\text{g}/\text{cm}^2$)
p-terphenyl $\text{C}_{18}\text{H}_{14}$	27.9	28.8	28.8 ± 1.2
perylene $\text{C}_{20}\text{H}_{12}$	61.7	58.3	59.4 ± 2.7

Table 1: Mass thickness of p-terphenyl and perylene thin films determined by weighing, from the quartz-oscillator thickness monitor and from the Bethe sum rule.