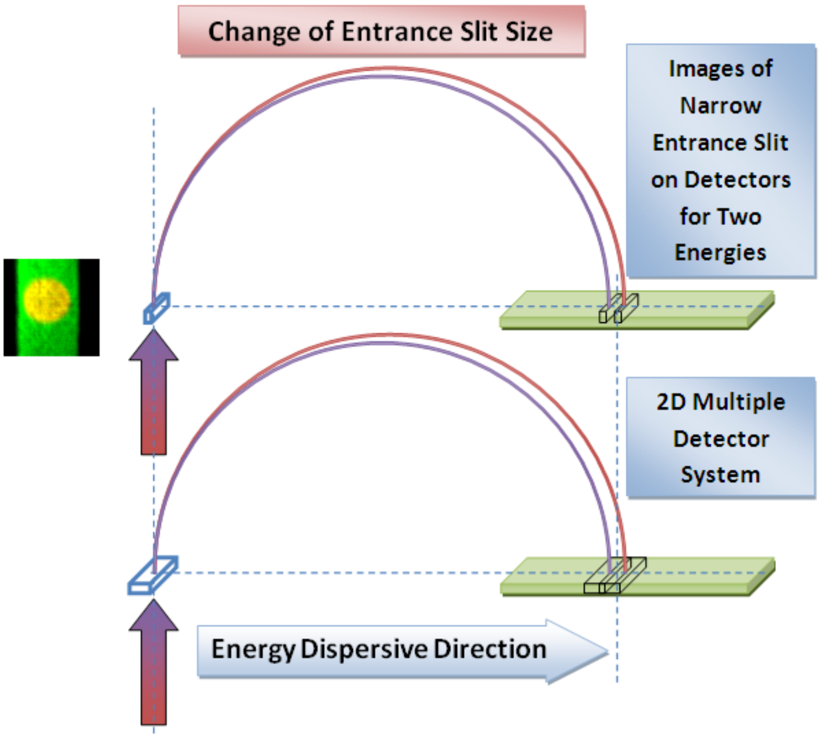
Test Peak Model: A Tool for Estimating Line Shape

This video looks at line shapes and how line shapes can be estimated from data.

The example used to illustrate how a line shape can be modified to reflect shapes in data via the Test Peak Model option on the Quantification Parameters dialog window Components property page is a Si 2p doublet. Data are measured using an acquisition mode optimised for quality of signal rather than for sensitivity. High sensitivity means high count rates which are achieved by compromising signal quality and therefore energy resolution. Quality of signal means restricting apertures allowing focused image quality signal to enter the hemispherical analyser (HSA) operating at low pass energy to provide maximum energy dispersion. The Si 2p doublet used throughout this video is recorded using medium magnification transfer lens mode limited to a 55um analysis area by a selected area aperture, the image of which projects signal spot of size equivalent to two thirds the width of the entrance aperture into the HSA. The silicon sample is assumed to be and evidence supports the assumption of a clean oxide free elemental silicon surface.



The shape modelled in this video is asymmetric in both Si 2p doublet components. The origin for this asymmetry is not entirely clear from these data, but the two most likely reasons relate to the semiconductor nature of Si 2p following a photoemission response observed in similar materials and/or these narrow Si 2p peaks include instrumental artefacts such as geometric aberration for HSA instruments that is a potential explanation of signal originating with a given energy but is recorded at a lower kinetic energy by the detection system. Regardless of origin, these doublet peaks provide an example where asymmetry in a synthetic line shape is an appropriate tool for estimating photoemission signal attributed to silicon.

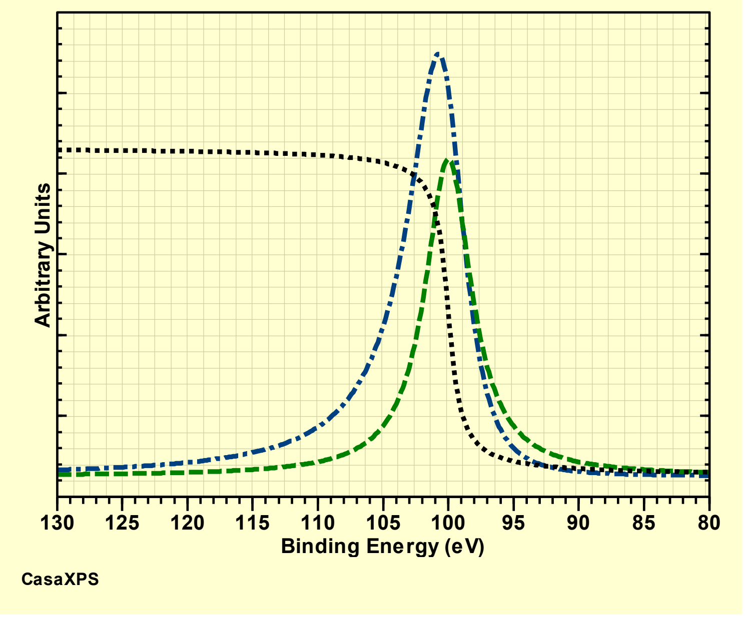
The line shape used to model asymmetry is as follows.

Underlying Asymmetric Lineshape:

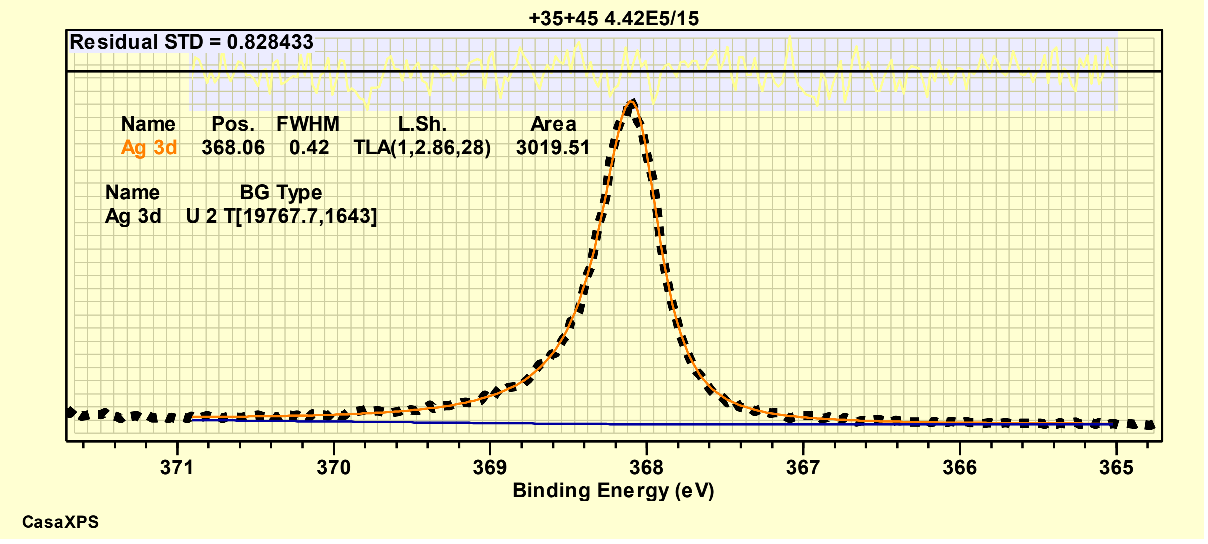
$$T(x:\alpha,\mu) = \left[\frac{1}{1+4x^2}\right]^{\alpha} \times \frac{1}{2}\left[\frac{\pi}{2} - tan^{-1}(2x) + \frac{\pi}{\mu}\right] \cdots \quad \mu > 0 \;\&\; \alpha > 0$$

Gaussian Modified Lineshape:

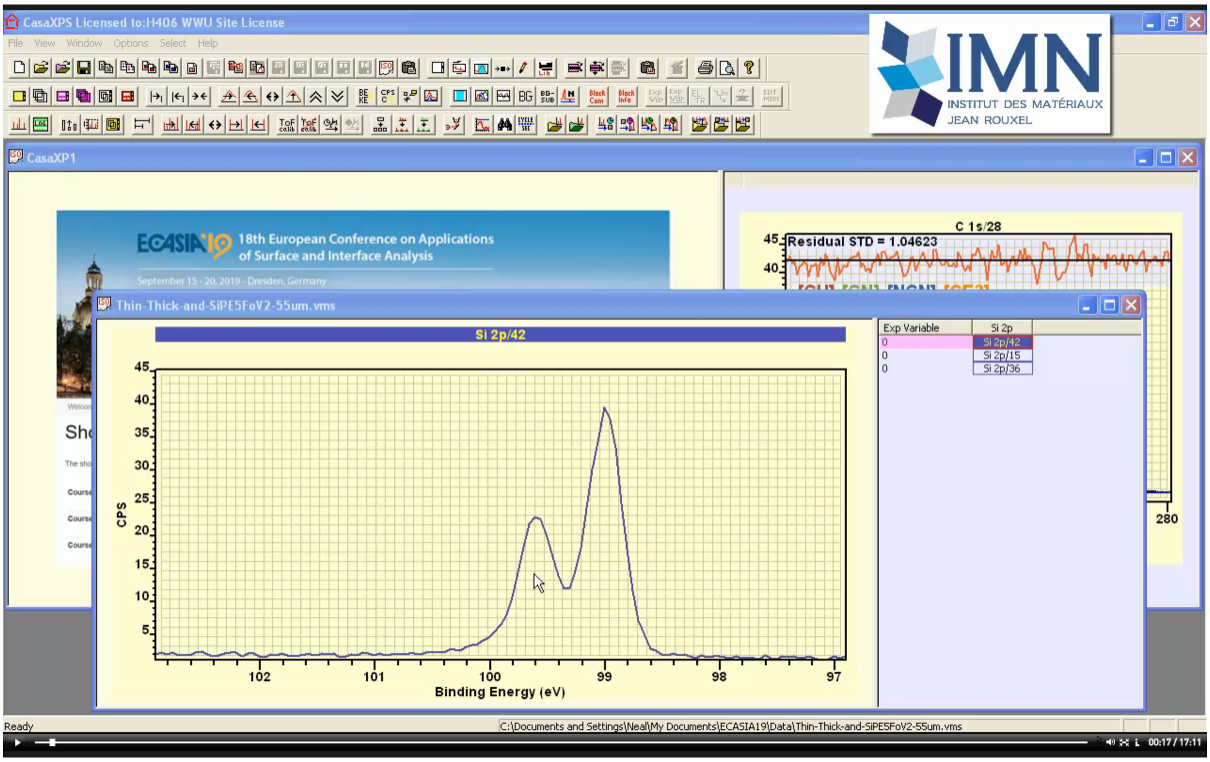
$$TLA(x:\alpha,\mu,\omega) = N\int_{-\infty}^{\infty} T(\tau:\alpha,\mu)g(x-\tau:\omega)d\tau$$



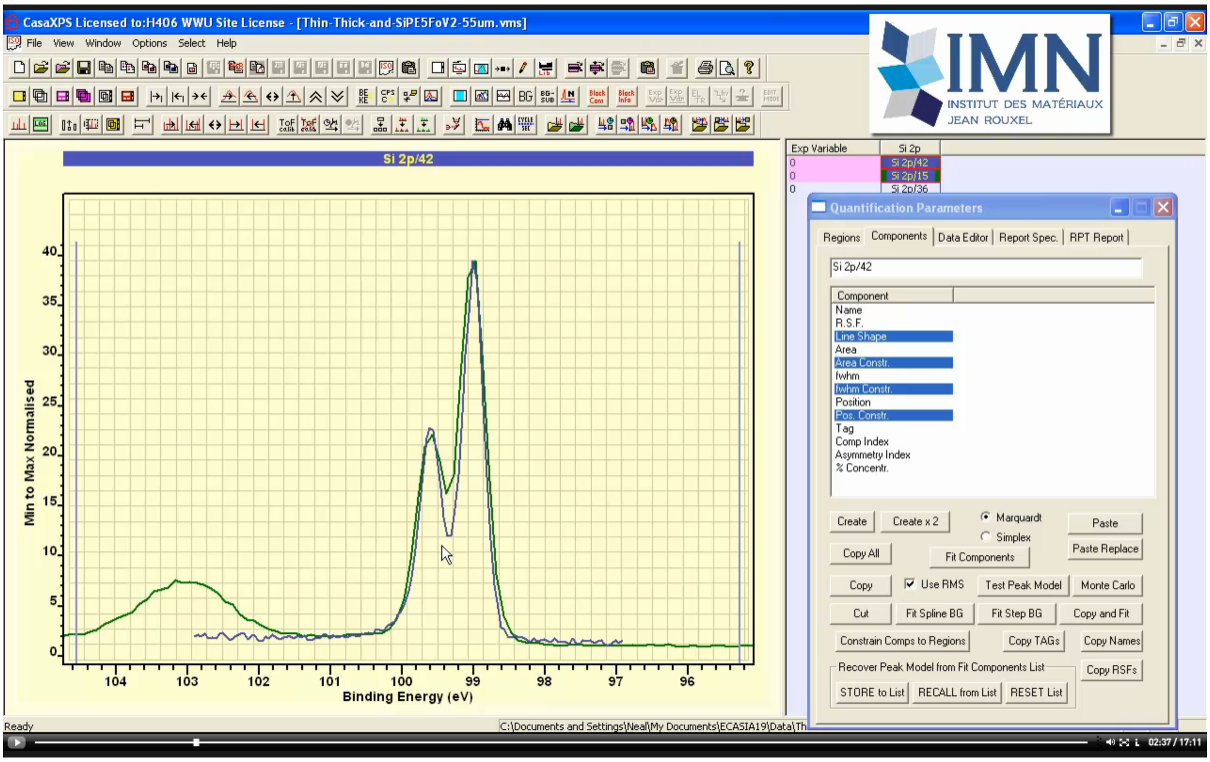
Step curve $\left[\frac{\pi}{2} - tan^{-1}(2x) + \frac{\pi}{\mu}\right]$ (dot, $\mu = 1$), Lorentzian $\left[\frac{1}{1+4x^2}\right]^{\alpha}$ (dash, $\alpha = 1$) and product of step curve with Lorentzian $\left[\frac{1}{1+4x^2}\right]^{\alpha} \times \frac{1}{2}\left[\frac{\pi}{2} - tan^{-1}(2x) + \frac{\pi}{\mu}\right]$ (dot/dash) (not drawn to scale).

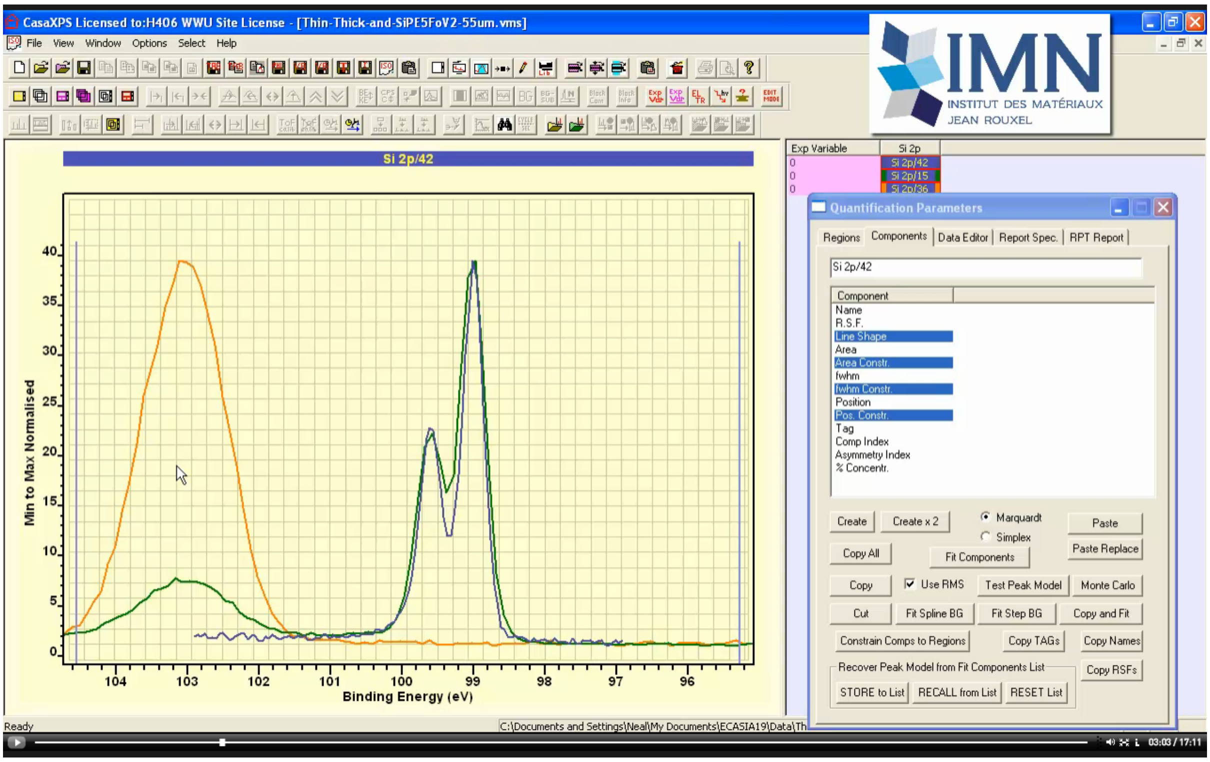


Ag $3d_{5/2}$ spectrum measured from Kratos Axis Ultra, PE5 in Hybrid lens mode using a limited and selected range of DLD logical detectors.

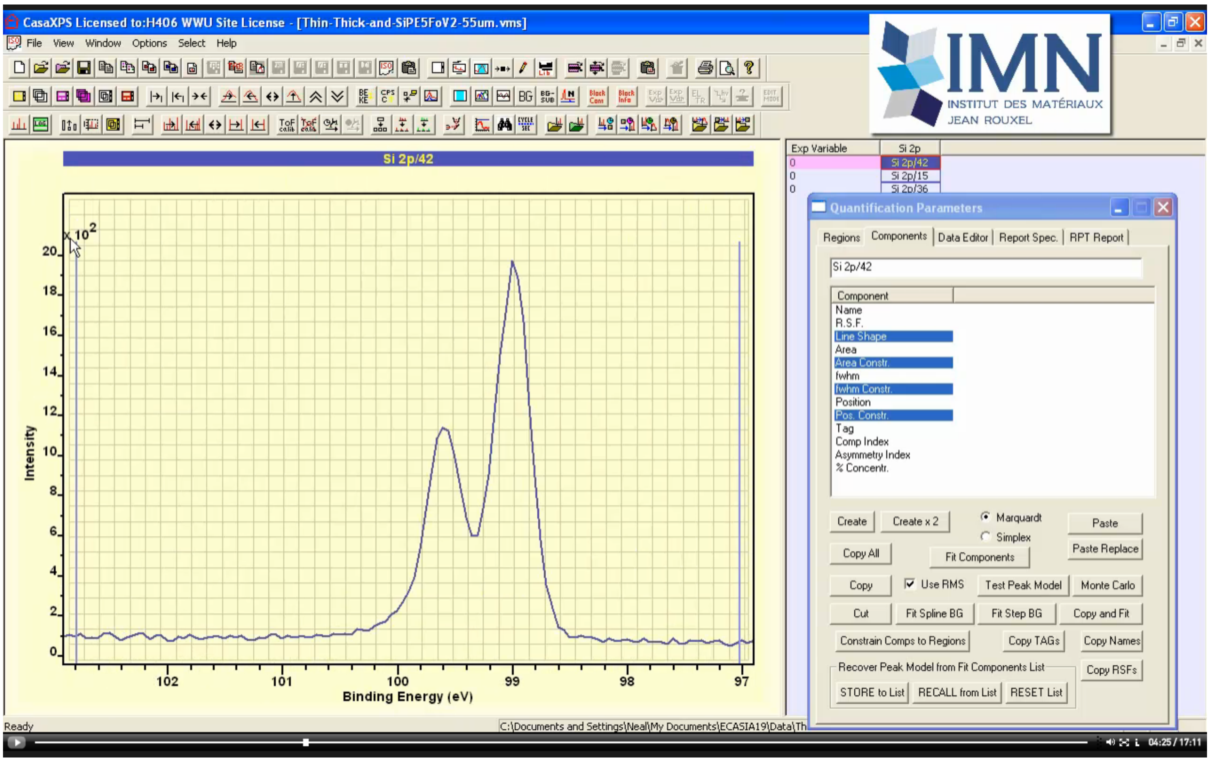


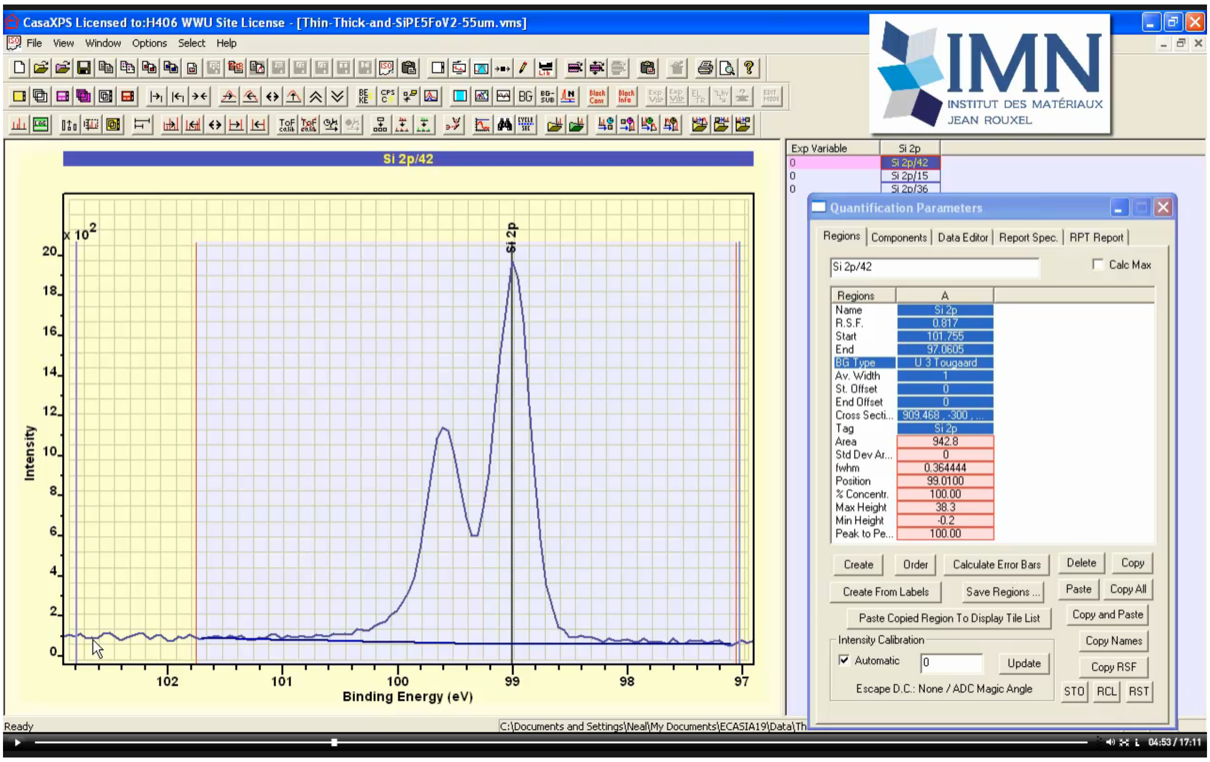
Si 2p represents a photoemission process slit by spin-orbital interactions into two component peaks. In this video data measured from a clean elemental silicon surface result in two energy resolved peak exhibiting asymmetry. The first task when considering data is the possibility peak shapes are the result of chemically shifted signal. Comparisons with samples similar to the clean silicon are made via Si 2p spectra as a means of estimating the potential influences of chemical state.



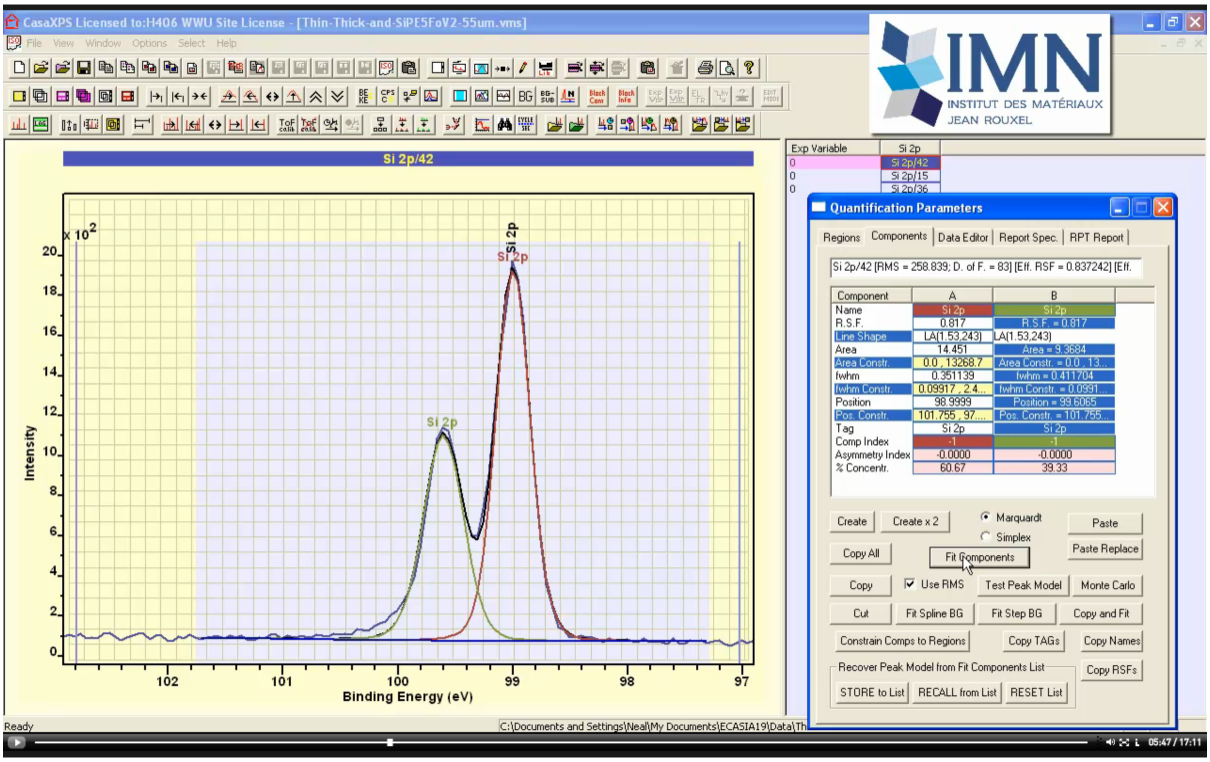


Si 2p data measured from clean silicon appears to be without significant oxide so the assumption is made that these peaks can be assigned to photoemission from silicon only.

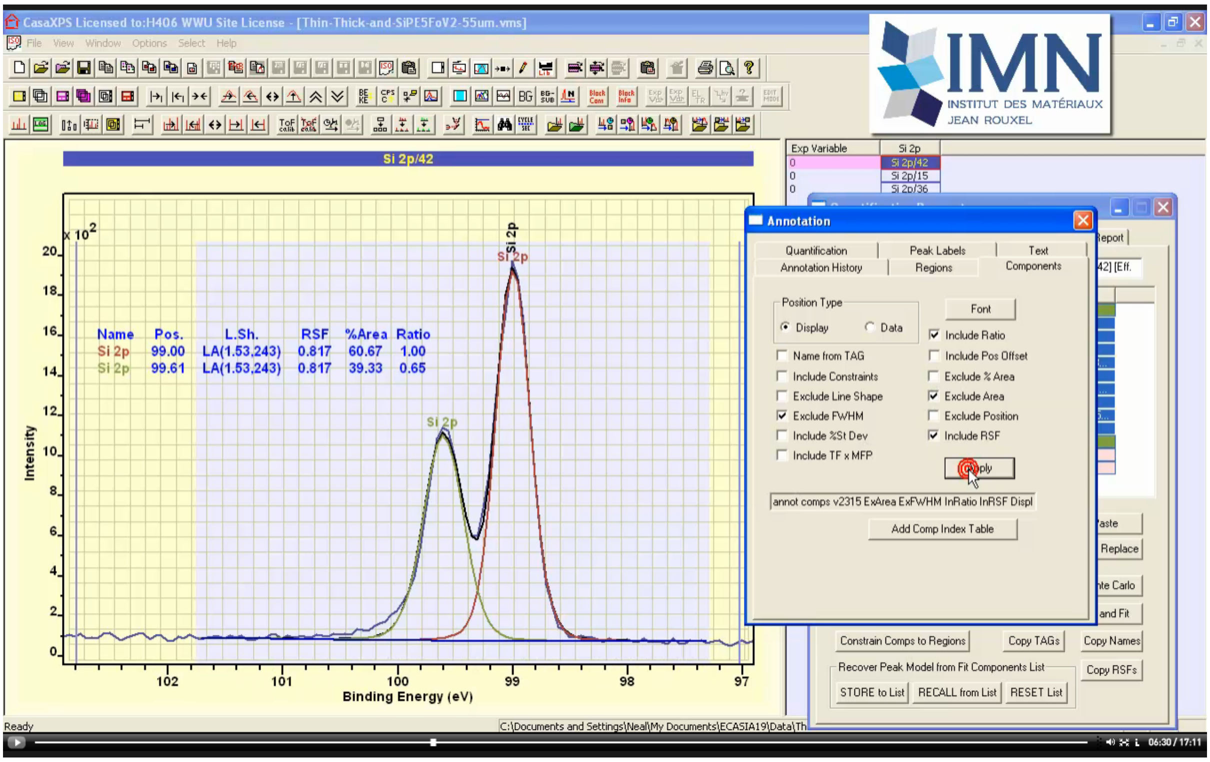




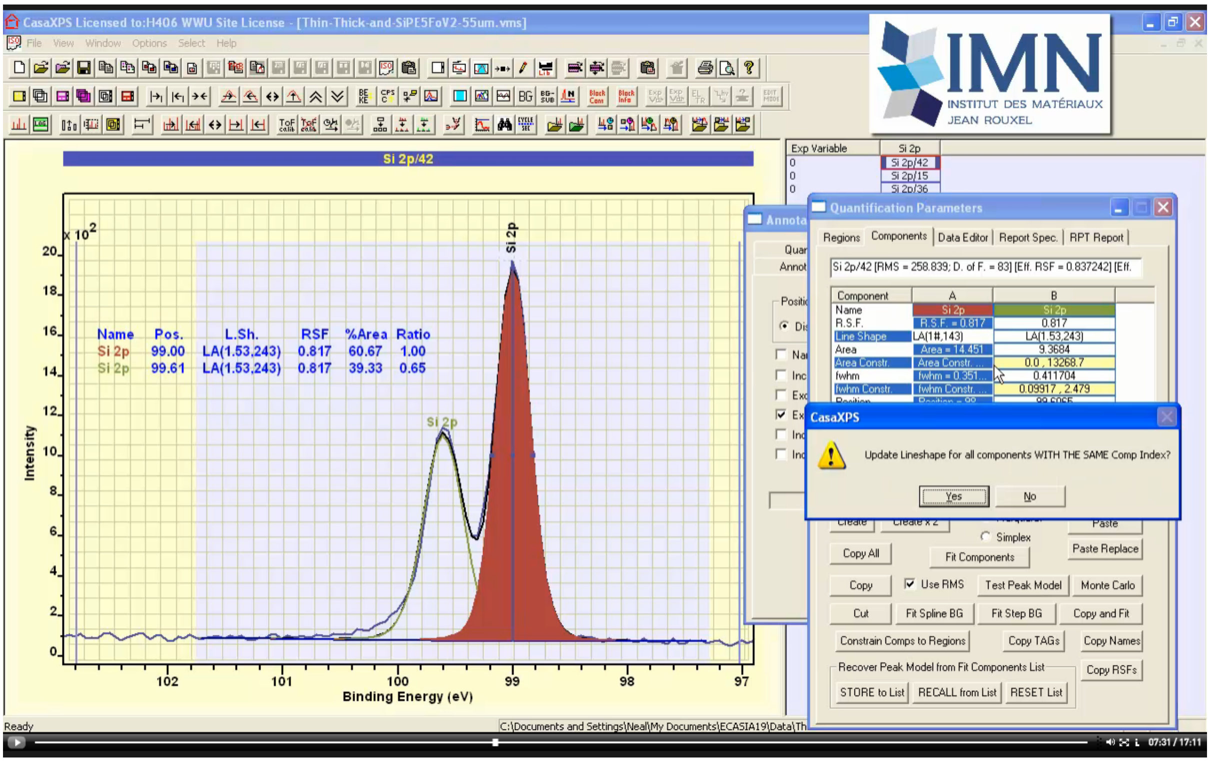
A single region is added to the VAMAS block containing Si 2p data from clean silicon. U 3 Tougaard background type is used to create an approximation to inelastic scattered background beneath Si 2p photoemission signal.



Initially, two component peaks with symmetric line shapes are added to the VAMAS block containing Si 2p data. These components when fitted do not produce expected data reproduction.



Adding an annotation table gathered from data displayed in the active display tile illustrates that these symmetrical peaks not only fail to reproduce these data the physical relationship between p-orbital photoemission doublets, namely, 2:1 intensity ratio is also less than perfect.



A more Lorentzian shapes lineshape is introduced in an attempt to model signal spread towards higher binding energy not accounted for by the initial line shape. A # character is used to copy the line shape entered in column A to the component in column B too.

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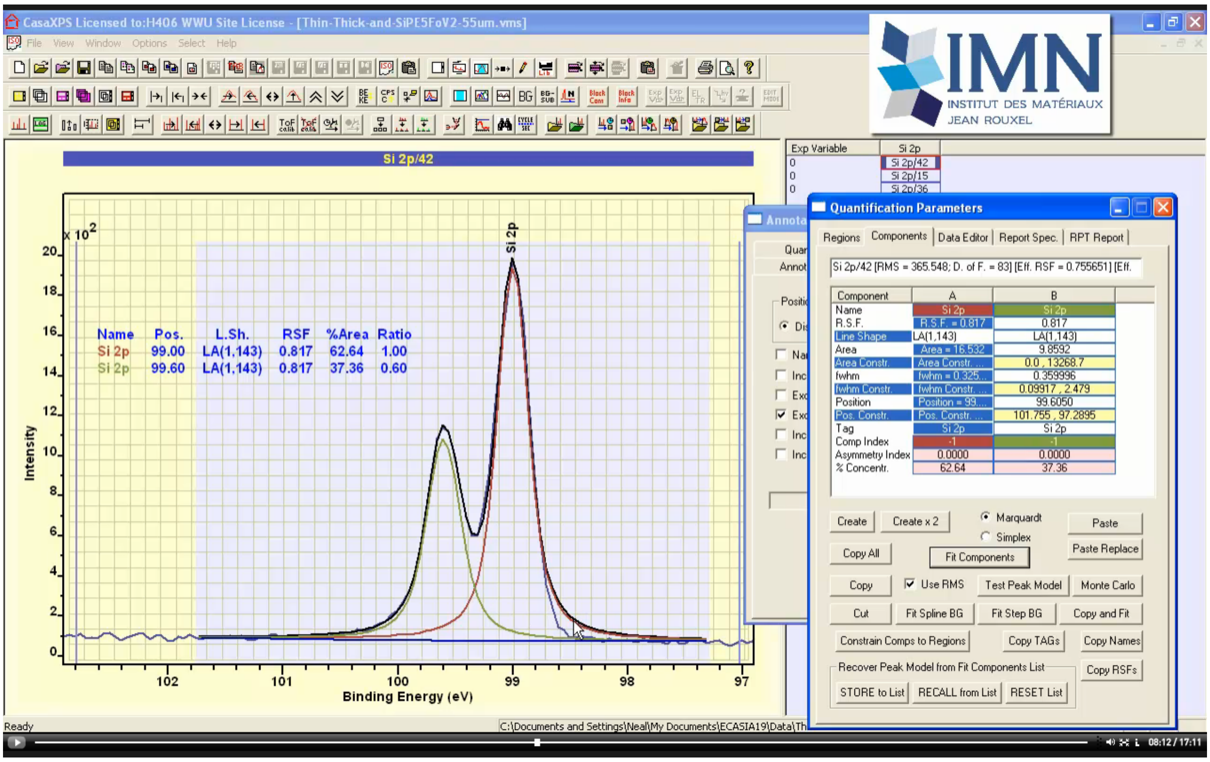
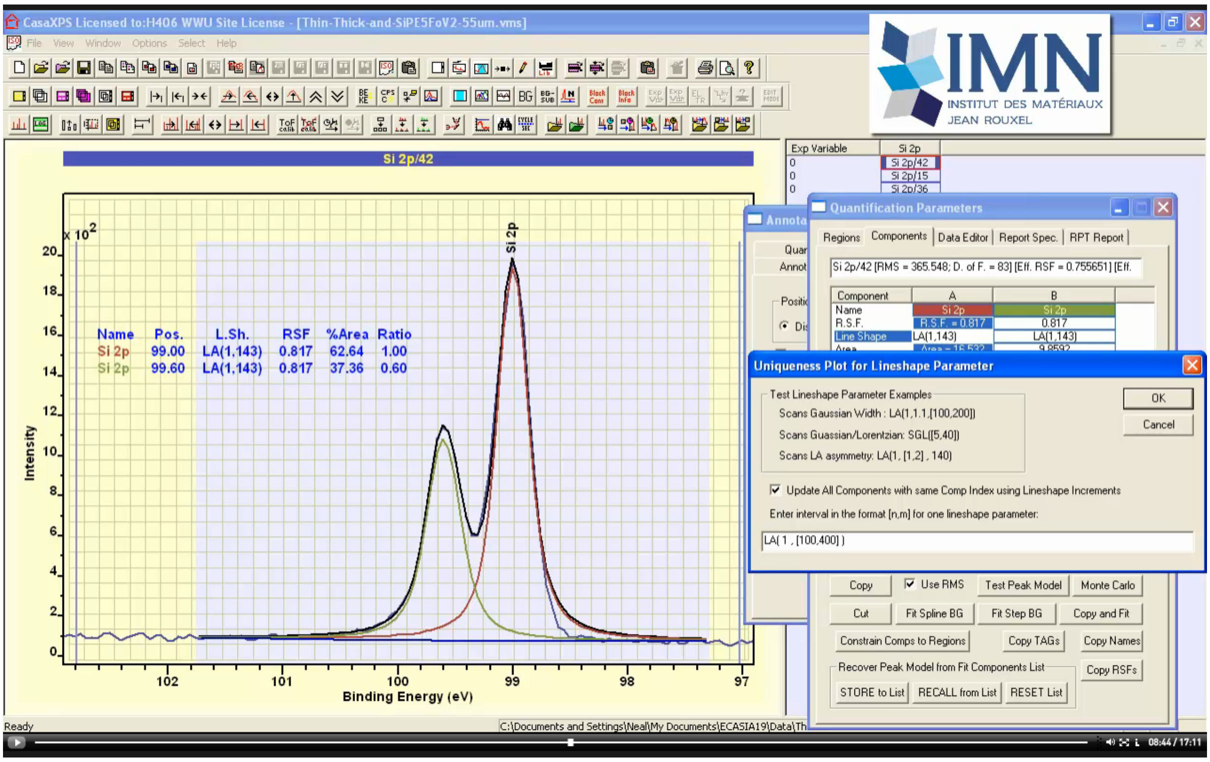
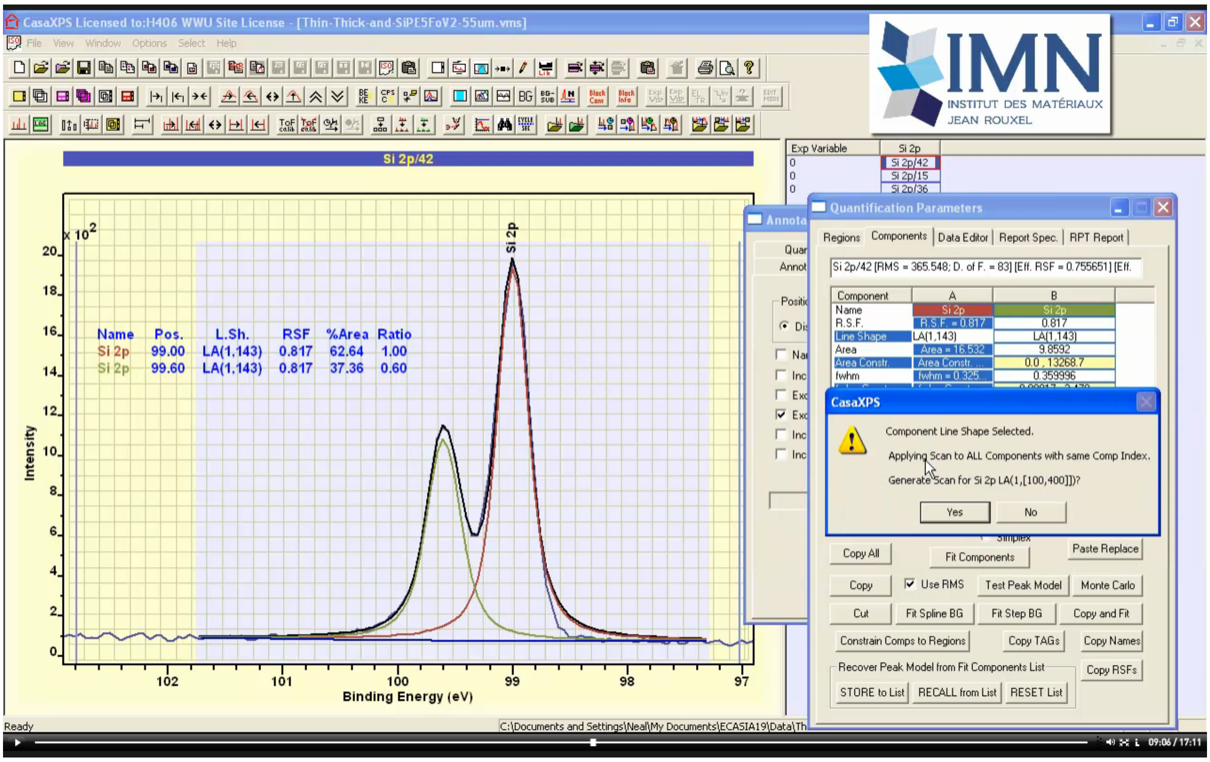


The new line shape, when fitted to these data, models peak maxima well and also accounts for signal to higher binding energy, but unfortunately introduces an error in terms of data reproduction to lower binding energy for these data.



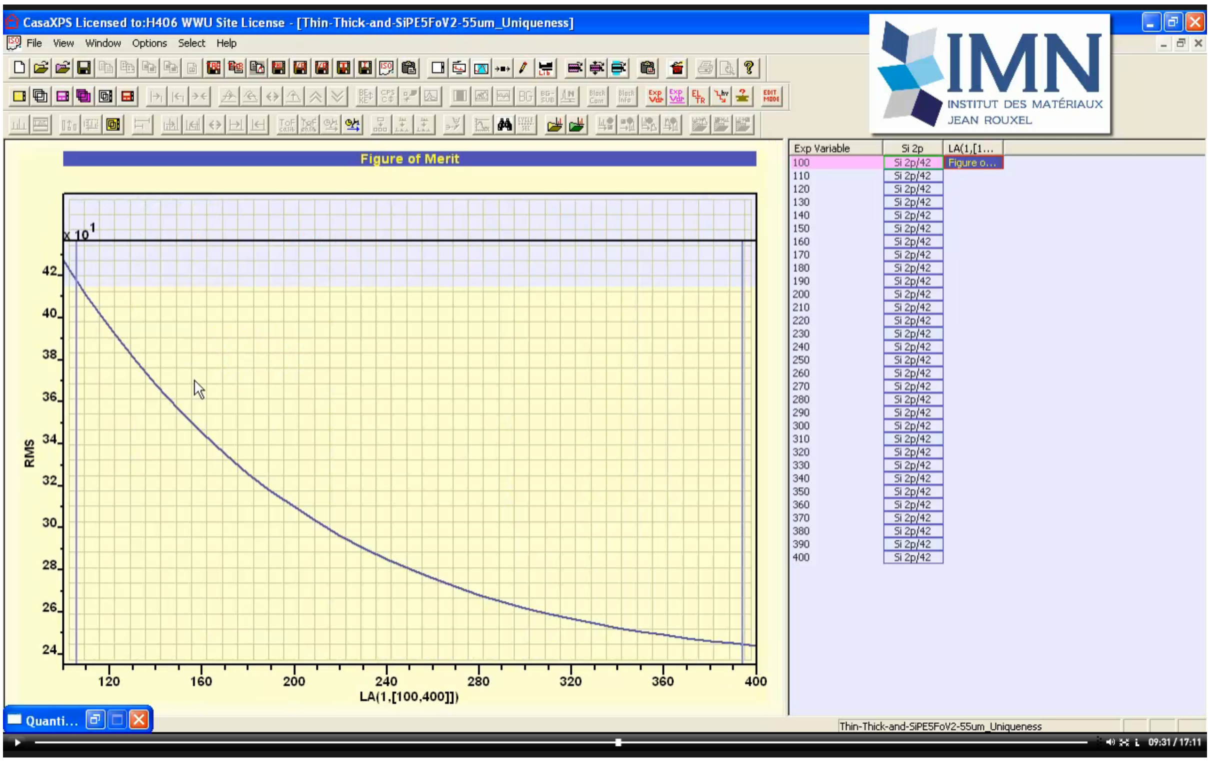
As a means of testing adjustments to the current line shape, the Test Peak Model button is made use of to scan a line shape parameter and perform a fit of the new peak model to Si 2p data. A line shape text-field is selected prior to pressing the button on the Components property page labelled Test

Peak Model. The result of such a line shape scan is a new file contain the original spectra fitted with a range of line shapes defined by adjustments to the parameter for which a value is specified using an interval within a pair of square brackets. The first example for the use of Test Peak Model is an interval for the Gaussian width parameter specified using the lineshape LA(1 , [100,400]).

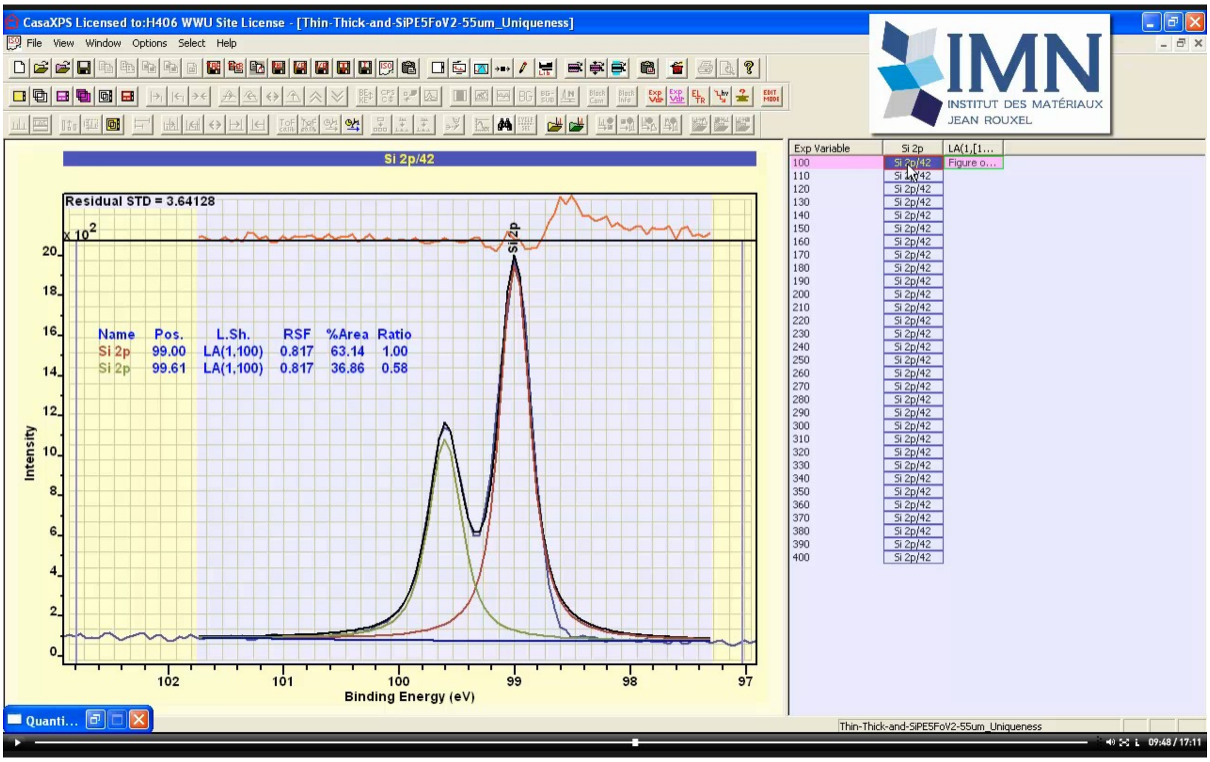


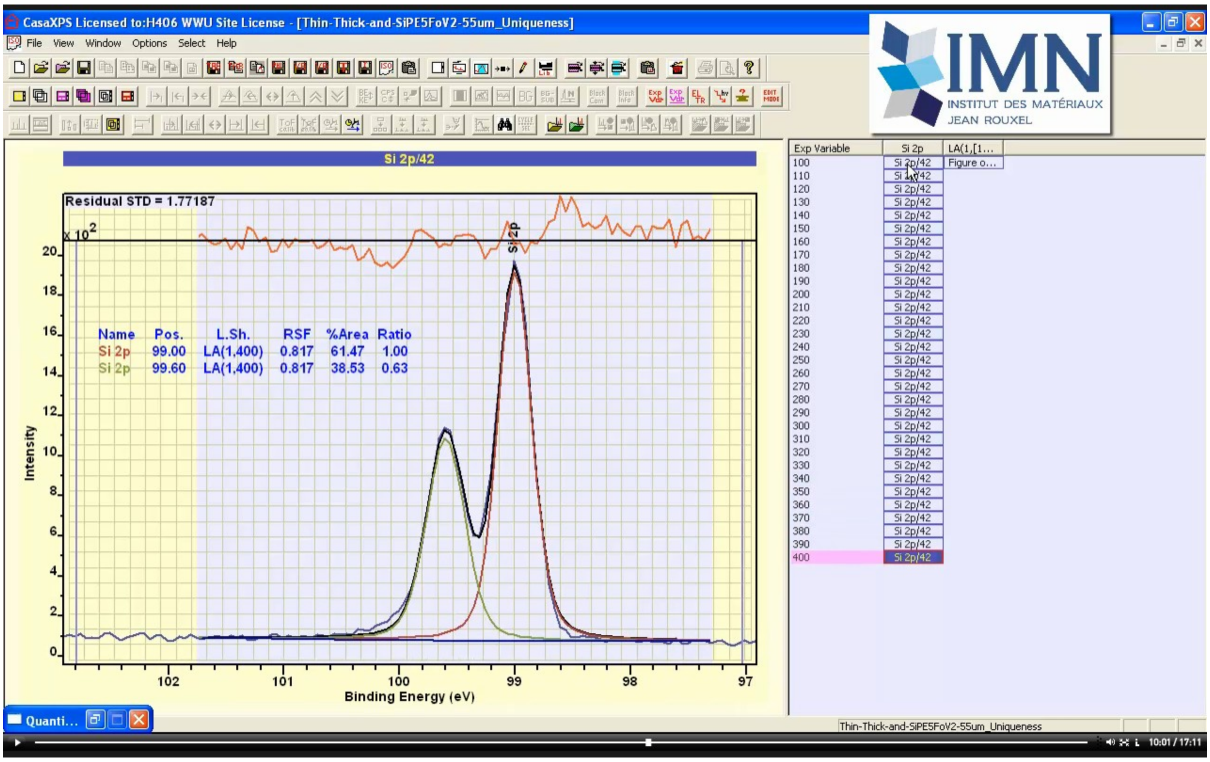
The result of scanning the Gaussian parameter is a plot for the figure of merit obtained by optimising the peak model including the new line shapes. Each spectrum fitted with a new peak model is also added to a new file. These spectra and fits of different peak models to the original spectrum is designed to allow line shapes and their influence on physical values to be assessed rather than simply relying on a figure of merit to identify the optimum choice for a line shape parameter.

Line shape parameters alter a very important property for a component peak that, when fitted as part of a peak model to data, significantly alters the physical parameters such as component binding energy or component intensity, both of which are typically significant to understanding sample chemistry. The property altered is the shape used to model photoemission signal and, in terms of optimisation, accurate photoemission shape represents the best chance of returning scientifically significant results by fitting components to data without user bias. A good figure of merit indicates good data reproduction but does not imply a correct peak model. Line shapes and the correct number of component peaks making use of correct line shapes and background fitted to data with a good figure of merit does imply scientific meaning can be assigned to binding energies and component intensities. A study of potential line shapes for a given sample and a given instrument is therefore an essential part of XPS data analysis based on the fitting of data by peak models.

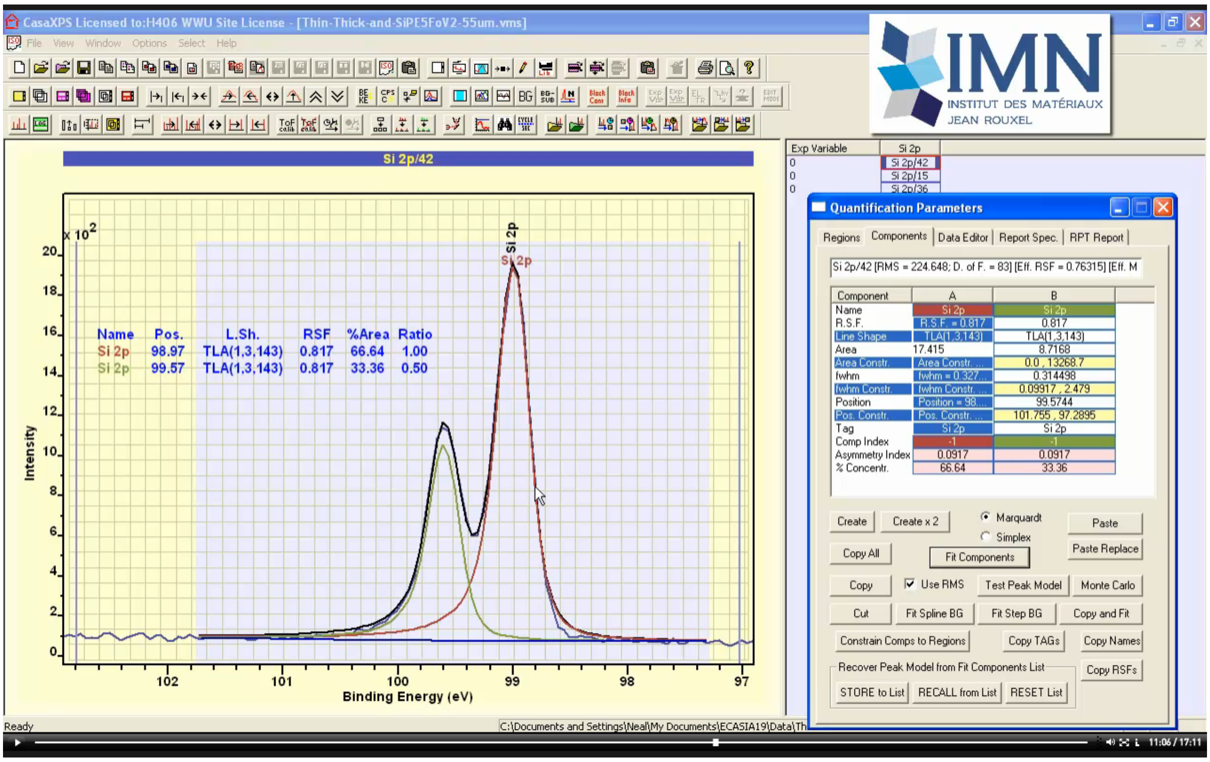


A figure of merit plot as a function of line shape parameter offers a tool for assessing changes induced by adjustments to a line shape parameter. However, observing the trend in terms of physical properties, such as the ratio for the p-orbital spin-orbit split doublet signal, is more important than the figure of merit. Scanning through these VAMAS blocks fitted with slightly different line shapes observing figure of merit, ratio of peaks and the way line shapes alter the fit to data provide guidance to best guess line shapes and subsequent line shape tests.

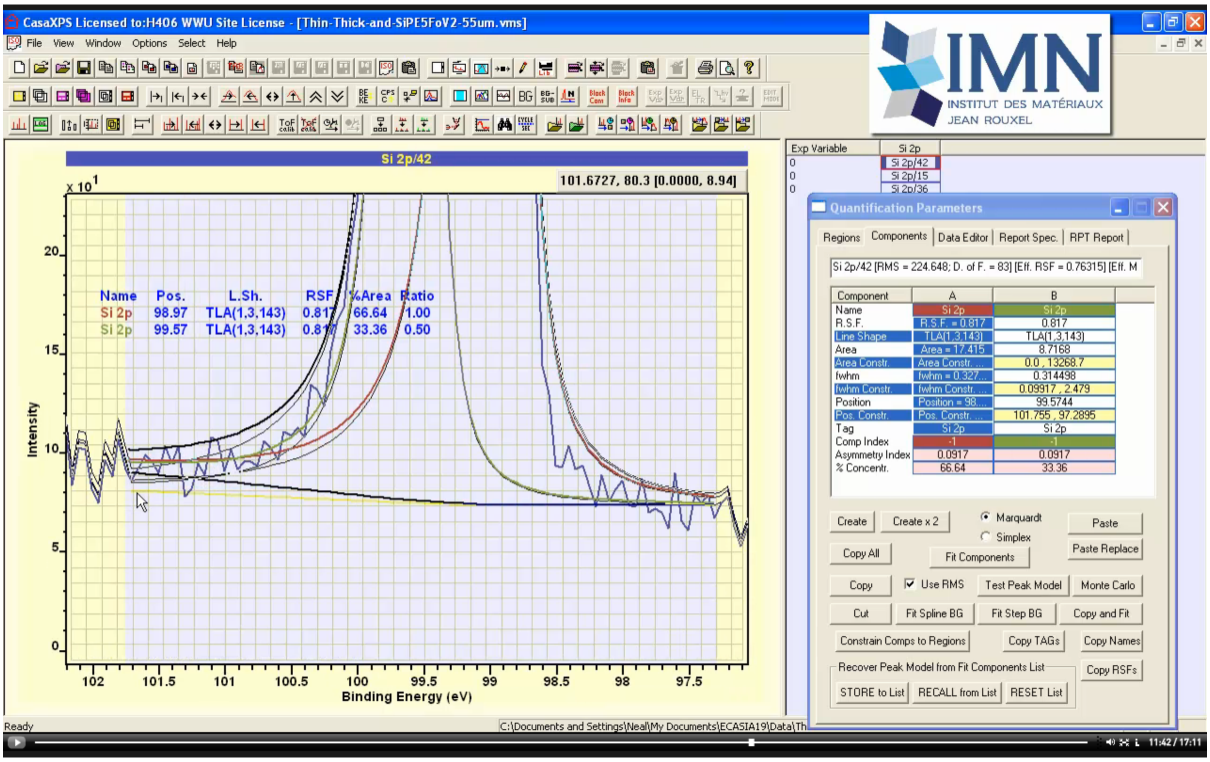




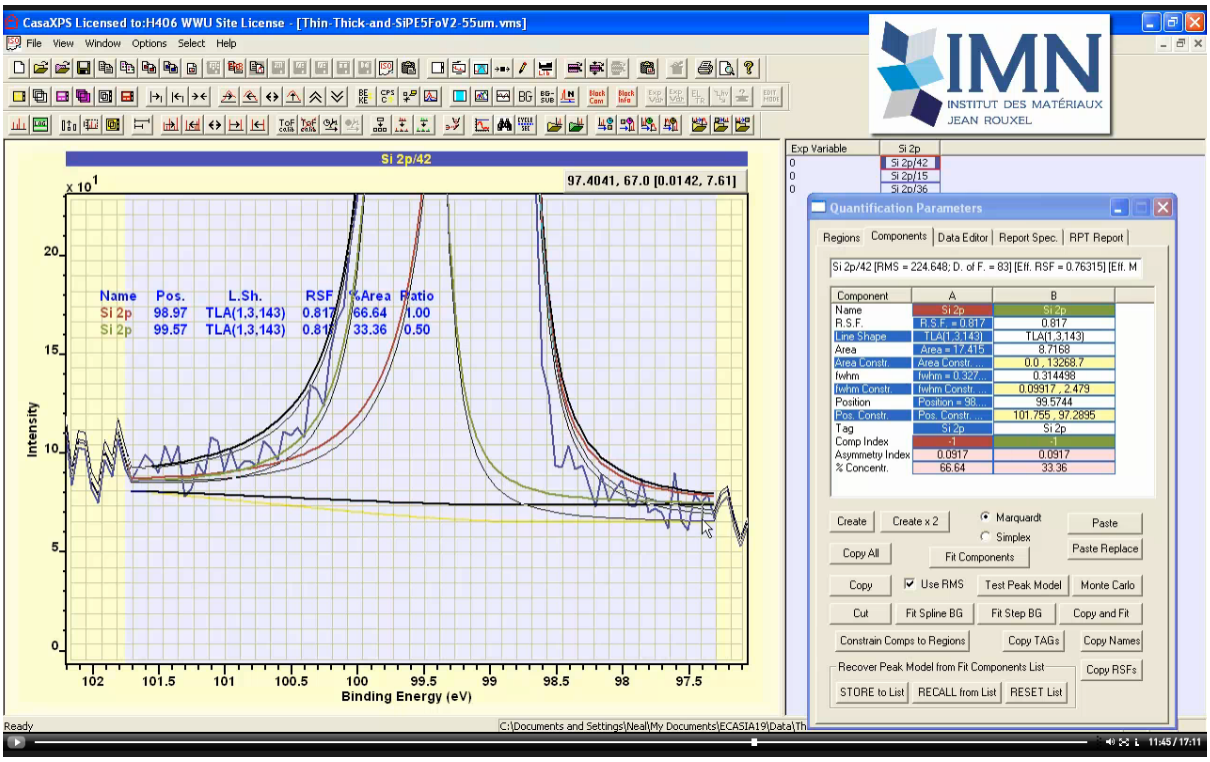
The first line shape within the scan and the last coupled with the shape for the figure of merit plot suggest the line shape is not best suited to fitting of these data using two component peaks.

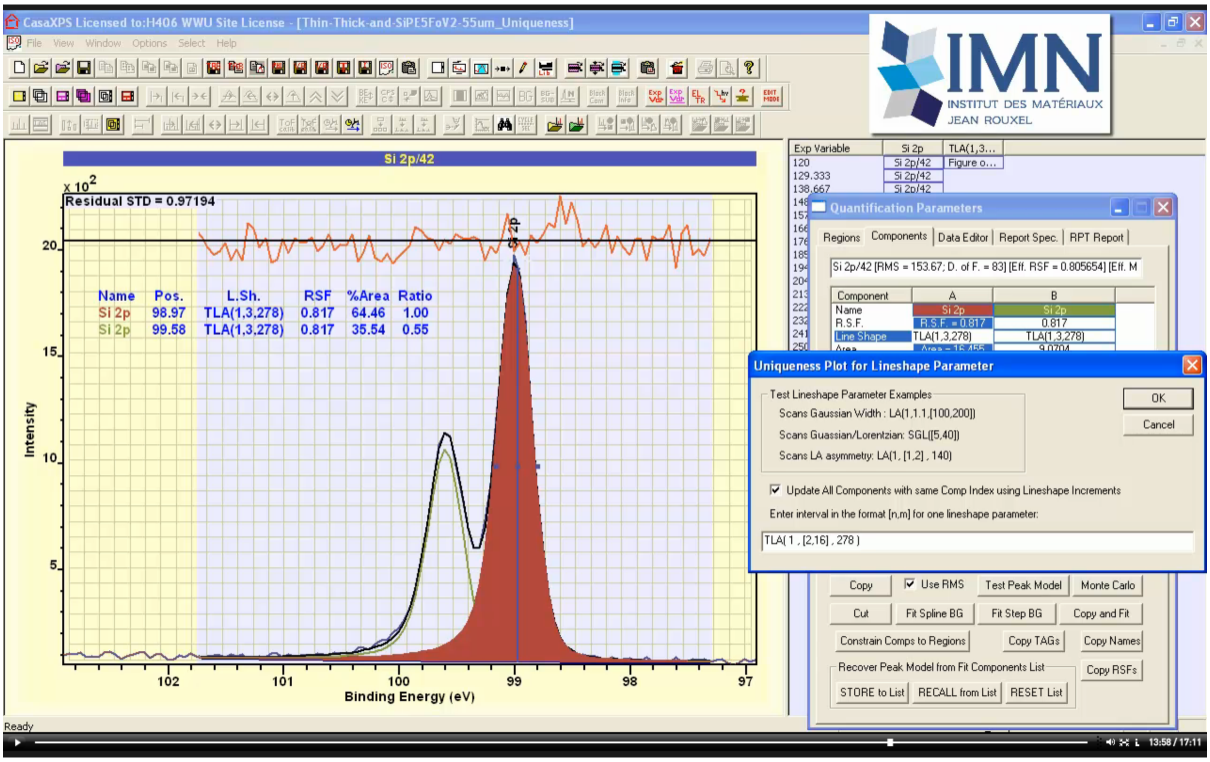


Returning to the original data using the Windows menu or simply closing the VAMAS file created by the Test Peak Model option allows a new line shape to be examined where the line shape is designed to accommodate asymmetry in a component peak.

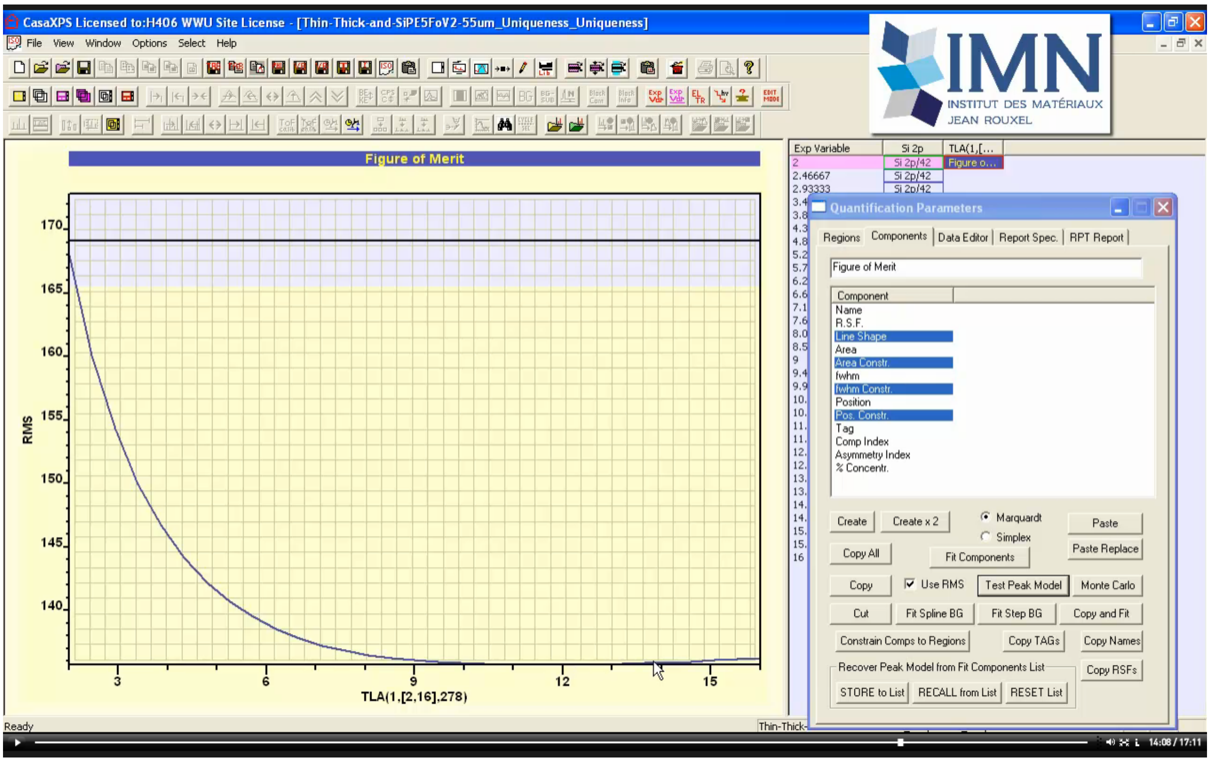


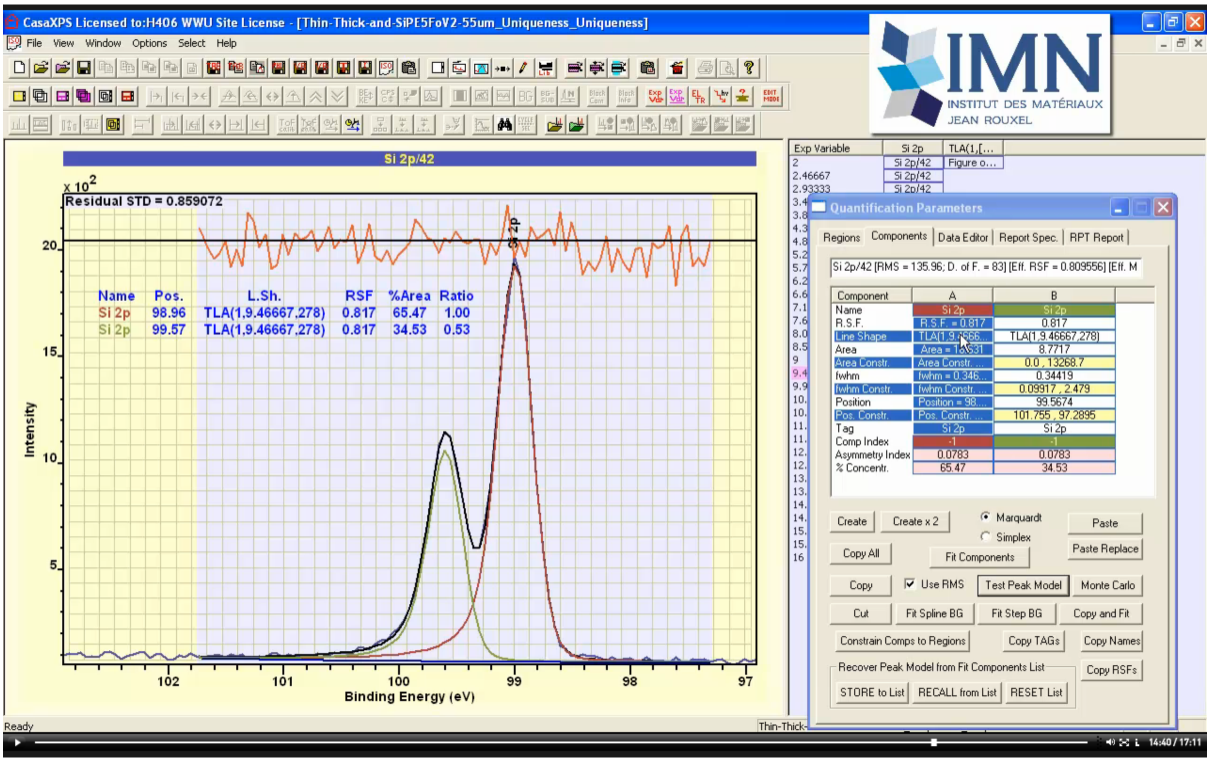
The logic behind the TLA line shape is a Lorentzian shape underpins photoemission peaks but when measured by XPS instruments and energy loss events associated with photoionisation signal, signal moves to lower kinetic energy compared to the energy for a purely Lorentzian process. What is more, a Lorentzian photoemission line models signal spread for the peak maximum and allowing a background to abruptly align with the perceived background is inconsistent with the use of a Lorentzian. Hence start and end offsets are used to allow the use of Lorentzian like line shapes.



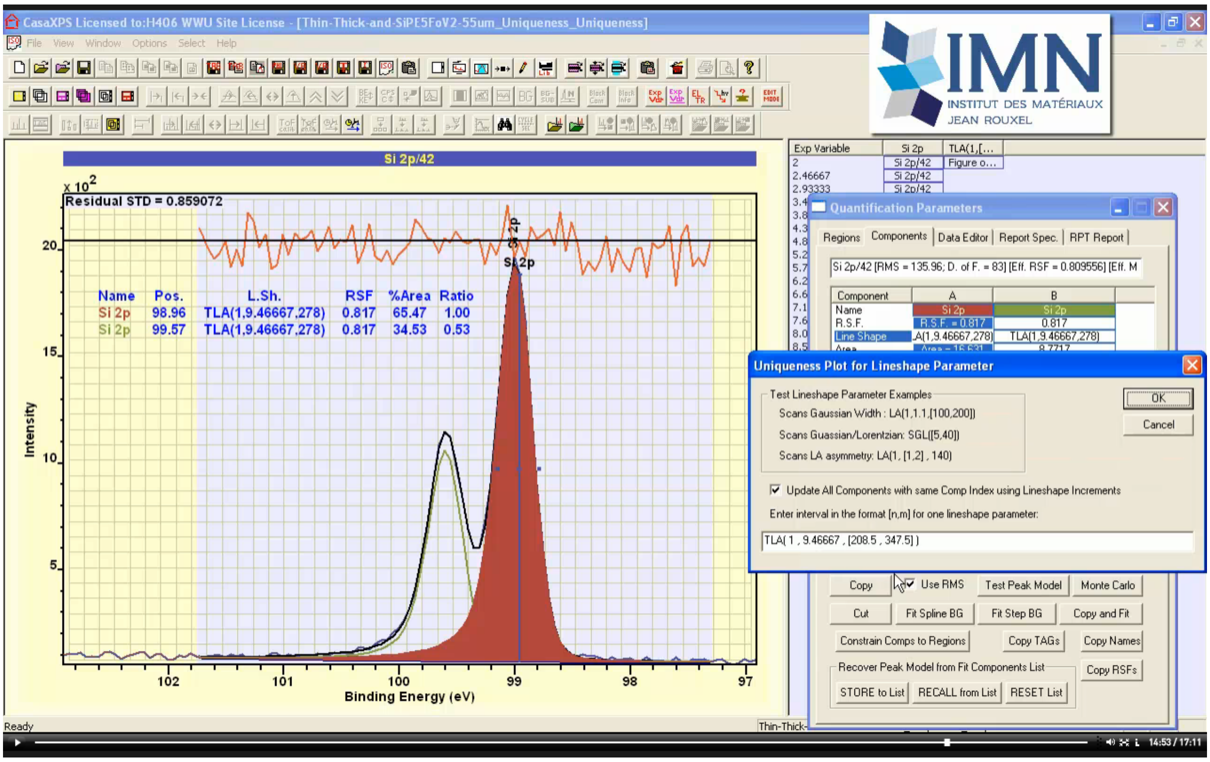


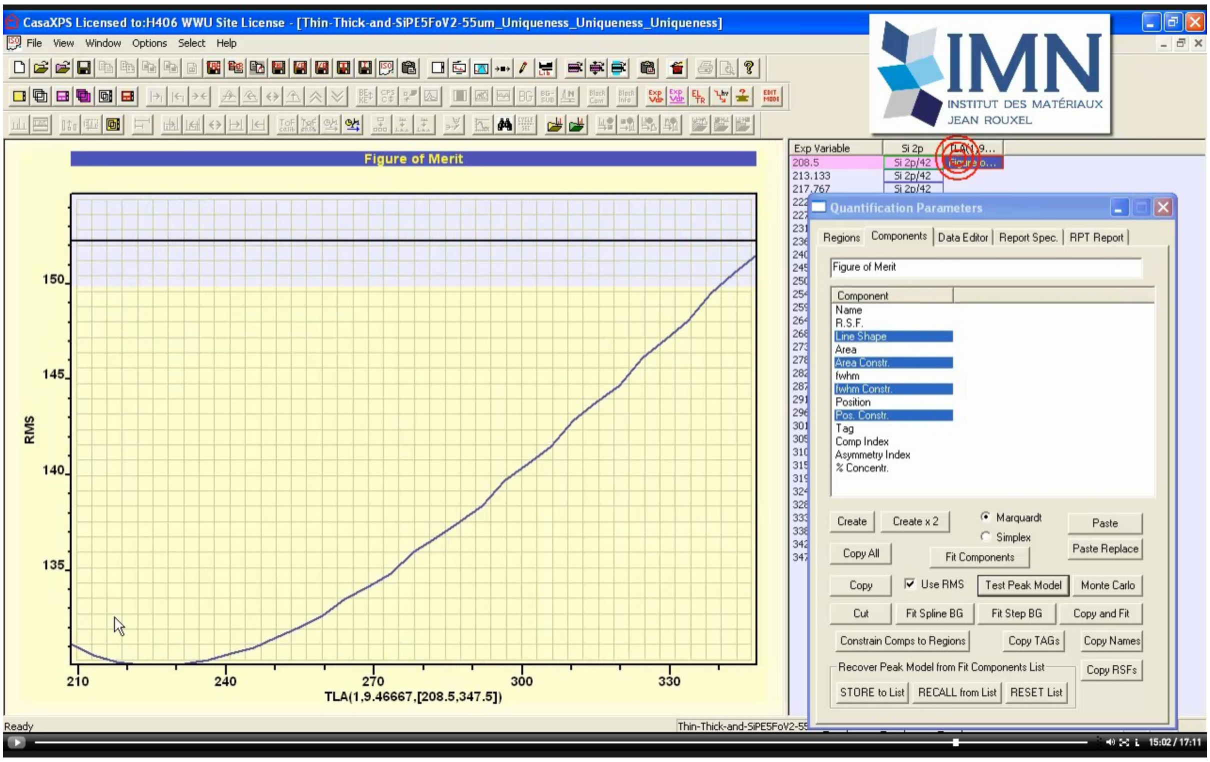
TLA line shape can be specified with three parameters. The second of these parameters alters the movement of signal from right to left side of a generalised Lorentzian resulting in an asymmetric line shape. Scanning the second parameter for a TLA line shape between 2 and 16 results in a figure of merit plot with a minimum but indices the parameter is not sensitive to a range of values close to the minimum.



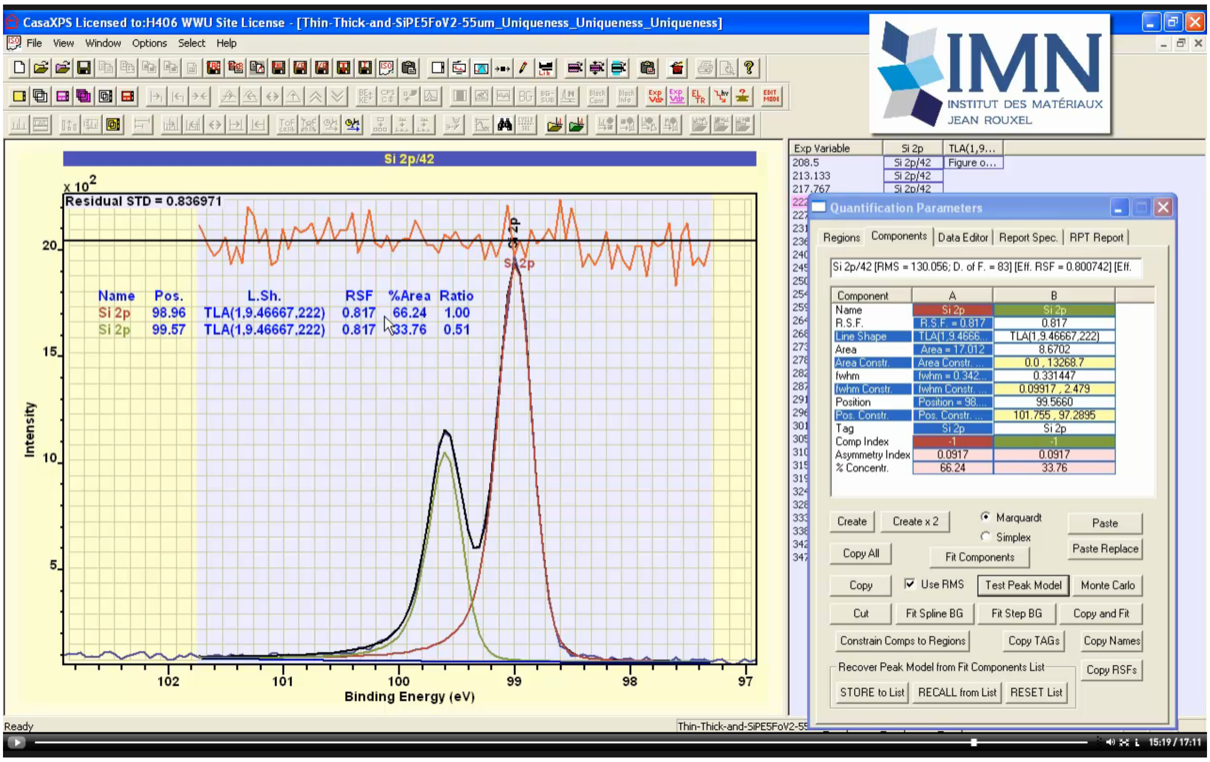


A new scan based on the Gaussian term in the TLA line shape making use of one of the results from the previous scan allows an investigation of adjustments centred around a promising values for the asymmetry parameter.

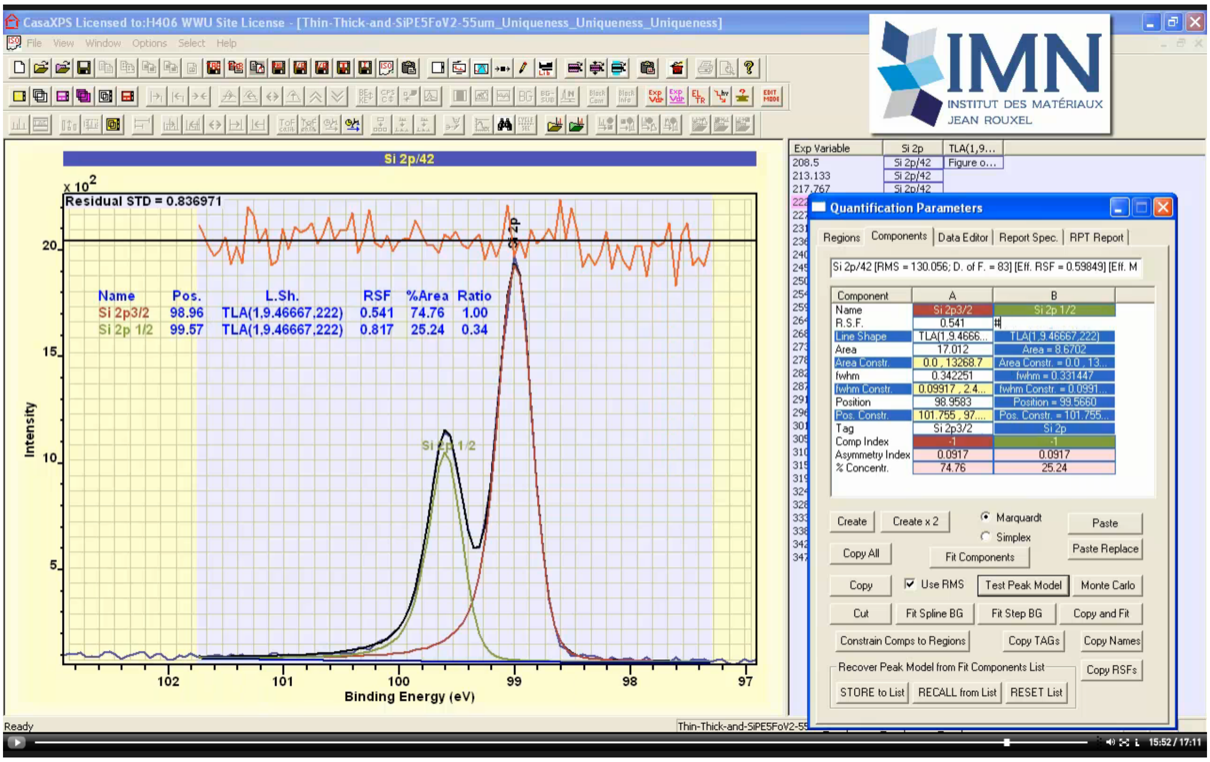




Ultimately these scans yield a line shape for which the figure of merit is consistent with pulse counted data collected using multiple detectors and the ratio for the doublet peaks matches expectation.



Si 2p peaks are nominally in the ratio 2:1 but are computed in terms of Scofield cross-sections to be slightly different from 2:1.



Updating the RSFs for individual doublet peaks with Scofield cross-sections allows a comparison in terms of component intensities consist with the probability for ionisation with different total orbital angular momentum in the final state. The result of applying these individual cross-sections to Si $2p_{3/2}$ and Si $2p_{1/2}$ component RSFs should be and does result in 50% to 50%.