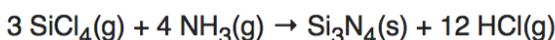
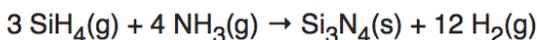
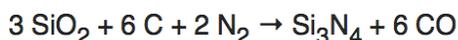
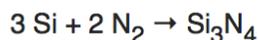


When is Si₃N₄ not Si₃N₄? When it is a Low Stress SiN_x Membrane Window

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The use of SiN_x windows has been well established as a support media which can be readily employed to observe microstructural evolution during a wide range of studies in the TEM/STEM and SEM's. It is a stable film which is usually grown on top of thin (100-300 μm thick) Silicon frames. SiN_x can be chemically treated, heated, and is relatively inert. Generally these films are grown using a chemical process and can be made routinely and reproducibly into films ranging from 10 nm to 1000 nm thick. There are a range of chemical synthesis methods which are used to grow these films which include:



The various chemical routes above all have been used to grow nitride films, however depending upon the route employed one can introduce stress in the films which for thin window application often results in rupture, particularly for the very thin self supporting windows which are used in electron microscopy. As a result one of the most common processes to create "low stress" nitride films involves a Low-Pressure Chemical Vapor Deposition (LPCVD) nitride process that uses dichlorosilane and ammonia. Chemically the process is suppose to create nominally pure Si₃N₄. As a practical issue, one finds that these films are not pure Si₃N₄, but rather also incorporate both Cl and O. In figure 1, is shown representative spectra taken from 2 different thickness of SiN_x films (50 & 200 nm), the chlorine is always present even after plasma cleaning and always to the same magnitude (~ 0.5%) relative to Silicon. Measured over multiple films from an individual supplier (thus fabrication process) the Si/Cl ratio is independent of thickness up to ~ 200 nm. This implies that the Cl (and O) are both incorporated into the SiN_x film during growth. In figure 2 is a comparison of the O and Cl signal from low stress SiN_x films procured from 4 different suppliers. All films tested contained both O and Cl but to varying amounts, which can be seen by the variable high of the Cl K peak), in addition, some of the films contain moderate amounts of Carbon.

While the amounts of Cl and O are small, their peaks can become problematic when the SiN_x film are used as nanoparticle supports during experiments which involve elemental microanalysis using either X-ray or Electron Energy Loss Spectroscopy. These media "system peaks" can be readily detected / observed and result in a spectral overlap of characteristic signal from small nanoparticles. For example, various L and M shell lines partially overlap the Cl K peaks (~ 2.6 keV). Fortunately the Cl/Si ratio appears to be constant for a given supplier, thus affording a method by which the single might be compensated for by scaling to the Si K signal.

It is therefore, important, during any microanalysis experiment to characterize the elemental composition of these film, prior to quantification. This also holds true for various “carbon” films which are purchased in bulk from suppliers, which also show contamination/incorporation of various atomic species such as O, P, Ca, K, depending upon the vendor and fabrication method.

References

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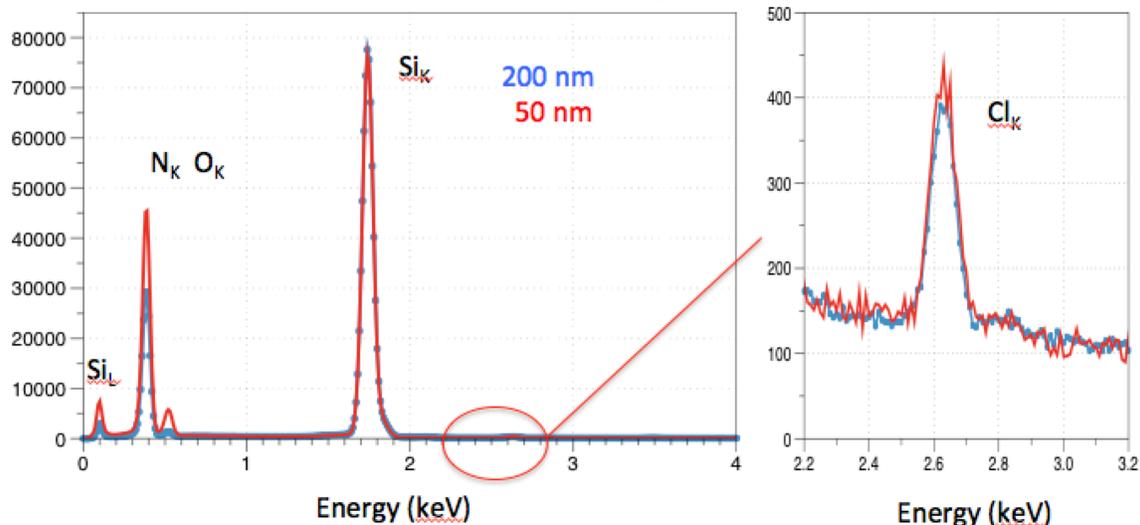


Figure 1.) SiN_x film showing Si_L, N_K, O_K, Si_K, and Cl_K x-ray lines, for two different film thicknesses normalized to the Si_K line intensity. Note the decrease in the N_K signal for the 200 nm film in this figure is due to x-ray absorption effects.

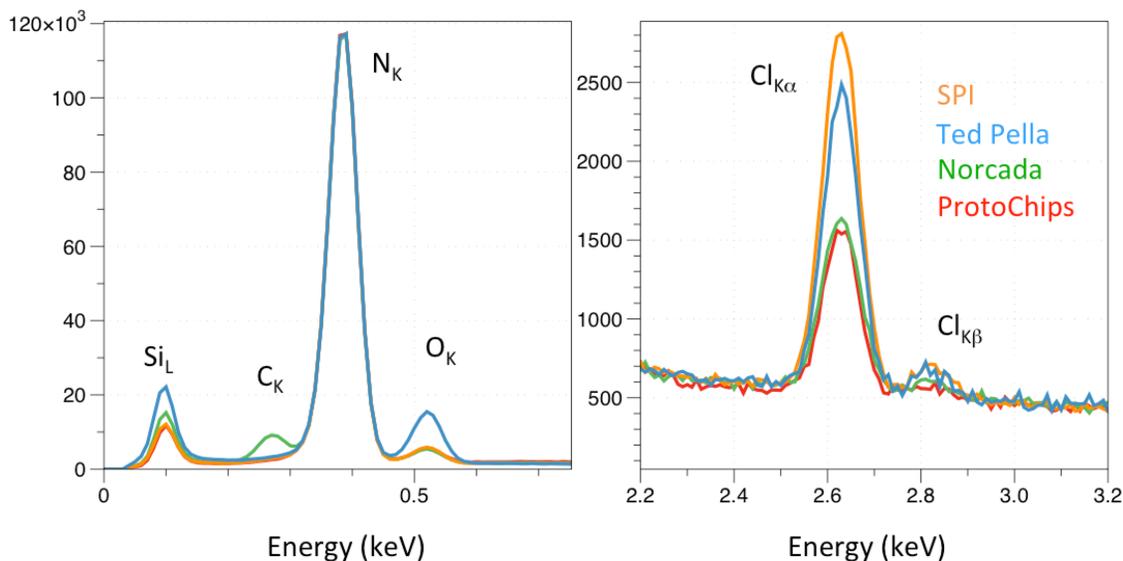


Figure 2.) SiN_x films from 4 different suppliers showing Si_L, C_K, N_K, O_K, Si_K, and Cl_K x-ray lines. Left spectra normalized at N_K. Right spectra normalized at Si_K