clusters produced by pyrolysis of silane onto holey carbon films. High resolution transmission electron images clearly shows nanoparticles with lattice planes surrounded by an amorphous oxide shell (Hofmeister et al., 1999; Laguna et al., 1999).

1.3.3 Electronic structure

Photoelectron spectra of silicon cluster anions have frequently been reported in the literature. These spectra exhibit rich features for small clusters, which become smoother as the clusters become larger. Maus, Ganteför and Eberhardt (Maus et al., 2000) assign the low binding energy features to the extra electron occupying the conduction bands. The higher energy features observed are attributed to the valence electrons. The energy difference between the two corresponds to the band gap in the bulk picture. Small clusters between n=3 and 13 were found to have band gap energies smaller than those typically seen for bulk crystals (Maus et al., 2000). This is incommensurate with the idea of quantum confinement, which would predict larger band gap energies for anything smaller than the bulk. The results were attributed to the entire geometric and electronic structure being affected by surface effects, similar to the reconstruction of the surface of bulk silicon crystals. While such an effect must clearly dominate the electronic structure of small clusters, the trend continues for larger clusters as well; Hoffmann et al., for instance, report the absence of a band gap for clusters up to 1000 atoms (Astruc Hoffmann et al., 2001b). For large Si cluster anions, the photoelectron spectrum is dominated by a single smooth and broad feature. The onset of photoemission shifts with size towards larger binding energies, a trend that is incommensurate with a bulk band gap picture and contrary to what one would expect from quantum confinement.

The observations made through photoelectron spectroscopy of cluster anions