A Computer Modelling Study of Perfect and Defective Silver (111) Surfaces

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Density functional theory calculations of the ideal and defective (111) surfaces of silver have shown that although the perfect surface shows very little atomic relaxation the introduction of vacancies, adatoms and step edges on the surface leads to significant bond distortions in the near−defect regions. The defective surfaces are not significantly less stable than the perfect (111) surface and the average calculated surface energy of 0.49 eV per surface atom agrees well with the experimental value of 0.55 eV/atom. Electron density contour plots show delocalisation along the surface compared to the bulk metal, while a more gradual decline of the electron density in the defect areas compared to the perfect surface leads to a more level electronic structure of the defective surfaces than their atomic structure. The formation energies of surface vacancies and adatoms with respect to gaseous silver atoms are +3.20 eV and −2.03 eV respectively, while the introduction of a step edge on the surface costs 0.42 eV per edge atom with respect to the planar surface. Adsorption of an adatom at the step edge releases 2.50 eV and the lower−coordinated edge sites, rather than the terrace sites of the planar (111) surface, are thus energetically preferred sites for further silver growth. Segregation of vacancies from the bulk material to the (111) surface is calculated to be exothermic at −0.18 eV per vacancy and recombination of a surface vacancy with a surface adatom will release 1.81 eV per vacancy/adatom pair. Preliminary calculations of the adsorption of atomic chlorine at the silver (111) surfaces are also presented.