Electrodeposition of Germanium from ionic liquids: nanoscale processes at the interface electrode / electrolyte

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The electrodeposition of germanium on flame annealed Au(111) films was investigated by Cyclic Voltammetry (CV) and in situ Scanning Tunneling Microscopy (STM) in the room temperature ionic liquid 1-Butyl-3- methylimidazoliumhexafluorophosphate containing GeX4 (X = I, Br, Cl) as germanium source. In all systems underpotential deposition of germanium is evident: upon bulk deposition from GeI4 the surface shows a remarkable reordering, and an almost disordered surface structure transforms to a layered structure on the time scale of about 1 hour with an averaged terrace height of 330 30 pm indicative of a (111) oriented germanium bilayer [1]. Upon partial oxidation random wormlike nanostructures form that heal on the time scale of about 2 hours [2]. From the GeCl4 saturated ionic liquid the overpotential deposition on the UPD layer starts with nanoclusters of 10 40 nm in diameter and some nanometers in height the typical dimensions of quantum dots. They can be stabilized for hours by proper selection of the electrode potential. In situ I/U tunneling spectroscopy of about 100 nm thick Ge films shows clearly semiconducting behaviour on the whole of the surface in the scanned area. The band gap of the bulk Ge determined by I/U spectroscopy is 0.7 0.1 eV, in good agreement with the theoretical value of 0.67 0.72 eV for bulk germanium at room temperature [3]. On a layer of approximately 20 nm in thickness we found both sites with semiconducting behaviour as well as sites with rather metallic behaviour. With dilute solutions narrowly dispersed Ge nanoclusters can be obtained that remain stable for at least one day in situ.

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