Electrodeposition of Germanium nanoclusters from an ionic liquid: an in situ STM/STS study

Frank Endres[1]

[1]University of Karlsruhe
Institute for Physical Chemistry
Karlsruhe D-76128
Germany

Nanocrystalline semiconductors are of great interest in basic research. Especially nanoparticles with diameters in the range of 1 - 20 nm play an important role because they exhibit a change in their electronic properties relative to that of the bulk material. With decreasing particle size the band gap increases, consequently the absorption threshold for light shifts to higher energies leading to a distinct blue shift. In many cases quantum confinement of the electrons and holes leads to a 1/r2 dependence of the band gap on the particle diameter. At the example of Ge nanoclusters made under Ultra High Vacuum (UHV) conditions this relationship has recently been shown [1]. In the last 15 years synthetic methods have been established that allow to make narrowly dispersed semiconductor nanocrystals and nanoclusters. The main interest focused on suspensions of such nanoparticles in which the photophysical properties could be investigated in detail. Quantum dots of semiconductors on different substrates made by molecular beam epitaxy (MBE) are also widely investigated nowadays in basic research, especially with local probe techniques like the Scanning Tunneling Microscope. Numerous studies have been published in the recent years, especially silicon substrates with different crystallographic orientations were employed for germanium deposition studies using MBE [2,3]. It was found that square pyramidical germanium nanoclusters of about 50 nm in side length and a few nm in height (quantum dots) on Si(100) show an interesting photoluminescence in the spectral range around 1 eV. These interesting optical properties make Ge quantum dots interesting for nanooptics. All the studies on Ge quantum dots were performed under Ultrahigh Vacuum conditions. It was recently shown by us for the first time that thin Ge(111) bilayers can be obtained by electrodeposition from the dry ionic liquid 1-Butyl-3-methyl-imidazolium-hexafluorophosphate that contained germaniumtetraiodide as Ge source [4,5]. This room temperature ionic liquid has in the pure state an electrochemical window of a little more than 4 V on Au(111). We dissolved GeI4 in a concentration between 0.1 and 1 mmol/l and could deposit Ge- films on Au(111) with a maximum thickness of about 20 nm. Upon partial oxidation random wormlike nanostructures were prepared that healed out on the time scale of about 2 hours in a complex process comprising electrodeposition / electrodissolution and periphery diffusion. If the ionic liquid is saturated with germaniumtetrachloride, Ge deposition on Au (111) starts in the UPD regime with the decoration of the gold steps by Ge at +1000 mV vs. Ge, then small islands that have initial heights of about 150 pm in the average start growing at +950 mV vs. Ge. At +750 mV vs. Ge islands with average heights of 250 pm form, they can be removed reversibly at higher electrode potentials and holes with apparent depths between about 30 and 100 pm remain in the gold surface for a short time. Still in the UPD regime a thin, rough Ge layer with metallic behaviour is deposited on the surface. It can be stripped reversibly upon rising the electrode potential to higher values. 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 microcrystalline germanium at room temperature. 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 lower concentrations of germaniumtetrachloride narrowly dispersed Ge nanoclusters can be obtained. Clusters with a thickness of 10 nm show a band gap of 0.7 +- 0.1 eV.

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