Electrodeposition of stable and narrowly dispersed germanium nanoclusters from an ionic liquid

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Germanium nanoclusters with a narrow height distribution have been electrodeposited from a dilute solution of $GeCl_4$ in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate $[BMIm]PF_6$: under the reported conditions the lateral sizes of most of the clusters range between 20 and 30 nm while their heights vary from 1 to 10 nm with most of them between 1 and 5 nm.

In the last few years the interest in ionic liquids as reaction media for chemical processes has considerably increased. Many combinations of cations and anions exist[1–3] and they have, depending on the ion-combination, wide electrochemical windows and negligible vapour pressures over wide temperature ranges. $[BMIm]PF_6$, for example, has an electrochemical window of a little more than 4 V on Au(111).[4] It is limited in the cathodic regime by the reduction of the organic cation while at the anodic limit gold oxidation sets in. Due to their wide electrochemical windows ionic liquids give in general access to elements, that can otherwise not be electrodeposited from aqueous solutions like *e.g.* Al, Ti, Si and Ge. Germanium nanoclusters and quantum dots with dimensions of only a few nanometers have been intensively investigated in the past in basic research. Such small Ge clusters show, for example, a photoluminescence[5] which is shifted to higher energies with decreasing particle size,[6] thus quantum size effects are present. Most of such studies were performed under ultrahigh vacuum conditions which would complicate a possible future nanotechnological process. Therefore we were seeking a method to prepare germanium by electrochemical means. In a recent study[7] we have reported in detail about *in situ* scanning tunnelling microscope (STM) results on germanium electrodeposition on Au(111). From $[BMIm]PF_6$, which was saturated either with $GeCl_4$ or $GeBr_4$, a thin Ge layer with a rather metallic behaviour and a maximum thickness of 300 pm forms before bulk growth sets in. Bulk deposition starts with nanoclusters and nanosized micrometer thick layers with a typical band gap of 0.7 ± 0.1 eV (shown by *in situ* tunnelling spectroscopy) can easily be obtained. However, from saturated solutions the growth of these nanoclusters is either too fast for size dependent studies, or the growth has to be surveyed for several hours *in situ* (by selecting the proper electrode potential) in order to perform the spectroscopic measurements 'at the right time'.

In the present communication we report that narrowly dispersed Ge nanoclusters can be made by electrochemical means on a reasonable time scale and that these clusters are stable even during permanent probing *in situ* with the STM.

Fig. 1 shows the cyclic voltammogram of $[BMIm]PF_6$ on Au(111) with $GeCl_4$ in an approximate concentration of $5 \pm 2 \times 10^{-3}$ mol l^{-1} ($v = 10$ mV s^{-1}, electrode area: 0.5 cm²), calibrated *vs.* the bulk deposition of germanium. The CV was acquired with the potentiostat that was delivered together with the employed STM controller (see below). Au(111) samples (gold on mica) were purchased from the Molecular Imaging Corporation and annealed at 900 °C under vacuum prior to use. Starting at 1 V, towards the cathodic regime the first peak at +250 mV is mainly correlated with the reduction of Ge(IV) to Ge(II). Furthermore, as with saturated solutions,[7] a thin rather

metallic Ge layer of 300 pm in maximum thickness forms on gold before bulk growth sets in at $E < 0$ V. The second peak is correlated with the electrodeposition of germanium from Ge(II) species, at -1 V reduction of the organic cation begins. On the basis of the present data we cannot comment on further intermediate Ge redox states. Platinum or tungsten electrodes can be used as the counter electrode, and we did not find any disturbance by products that are formed at the counter electrode. Pt was used as a 'quasi' reference electrode, and it gives a sufficiently stable electrode potential as soon as a certain amount of Ge(II) is formed, provided the solution does not contain water. At $E > 1$ V gold oxidation sets in, starting at the steps between different Au(111) terraces. In part the oxidation peaks at $E > 1$ V are also due to Ge oxidation. From the cyclic voltammogram the deposition of Ge seems to be irreversible as there is no clear stripping peak. Such irreversibility has also been observed for Si, which has been electrodeposited from $SiCl_4$ in organic solutions.[8] Nevertheless Ge can be removed completely from the surface. It is known that Ge(IV) halides attack elemental Ge in a chemical reaction (Ge + Ge(IV) → 2 Ge(II)[9]) and with respect to electrooxidation this process seems to be kinetically favorable. More details on this dissolution/ electrodissolution can be found in refs. 4 and 7. The two Ge reduction peaks are mainly controlled by diffusion as the peak currents rise linearly with the square root of scan rate (see also ref. 10).

The *in situ* STM experiments were performed with a Molecular Imaging PicoScan STM controller in feedback mode under potentiostatic conditions with in house built STM heads that allow measurements under inert gas (H_2O and O_2 below 2 ppm).[11] Typical setpoints for the STM measurement are in the range 1–2 nA while for the semiconductor nanoparticles probed here the tunnelling voltage should be at least +500 mV. Fig. 2(a)–(c) show germanium nanoclusters on Au(111) as probed *in situ* by the STM. They were made in the following way: with retracted tip (in order to exclude any influence of the tip on the deposition process) the electrode potential was set from the open circuit value (about 1 V *vs.* Ge) for 1 h to -300 mV *vs.* Ge, and held constant Then the tip was approached with a bias of
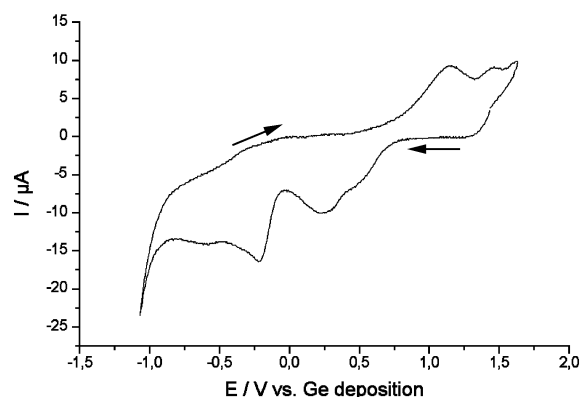

Fig. 1 Cyclic voltammogram of $[BMIm]PF_6$ on Au(111), $c(GeCl_4) = (5 \pm 2) \times 10^{-3}$ mol l^{-1}, $v = 10$ mV s^{-1}.

+600 mV and a setpoint of 1 nA. The same parameters were used for the STM scan. The feedback loop was adjusted such that it reacted rapidly but without tending to oscillation. Fig. 2(a) shows the surface about 1 h after the electrodeposition had been started. It is obvious that many clusters with different sizes have been deposited on the surface. Fig. 2(b) shows the same site 8 h later, Fig. 2(c) shows the surface 16 h later, the surface being permanently probed with the STM, taking 30 min to complete one image. Essentially, the clusters neither grow nor shrink considerably under the applied conditions, only a new cluster (marked by a white arrow in (b) appears on the surface. Analysis of the intermediate images shows that this cluster was deposited spontaneously from one scan to another one, maybe it was induced in part by the STM tip. A height statistics of the pictures (Fig. 2(d)) shows that most of the clusters have a height between 1 and 5 nm with a few ones up to 10 nm. In order to prove that elemental germanium was deposited we performed *in situ* current/voltage (*I/U*) tunnelling spectroscopy on the large clusters 1–4 in Fig. 2(b), that have heights of about 10 nm. The tip was positioned over the site of interest and a tunnelling
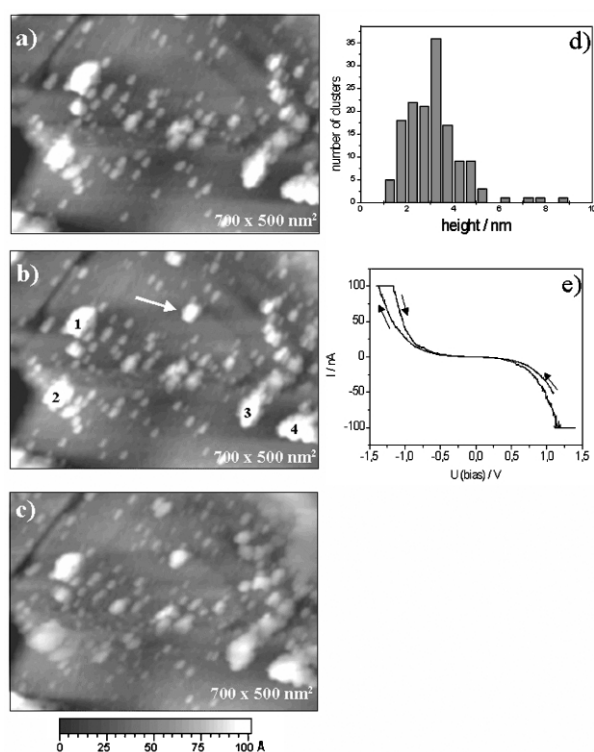
voltage of 1100 mV as well as an initial setpoint of 50 nA were applied. Then the feedback was switched off and immediately the bias scan of approximately 2 s duration was run. A typical tunnelling spectrum is shown in Fig. 2(e), and we measured a band gap of *ca*. 0.7 ± 0.1 eV, which is—within the limits of error—close to the value of 0.67 eV for microcrystalline germanium. Interestingly, with decreasing thickness the band gap of the clusters rather seems to decrease than to increase. These studies—also conducted on different substrates such as Si(111) and highly oriented pyrolytic graphite—are still under progress and will be reported later. If the $GeCl_4$ concentration is reduced to 0.1 mmol l^{-1} and lower, the growth of the Ge can be further slowed down. The parameters for electrodeposition of the Ge nanoclusters are not yet optimized with respect to the concentration of $GeCl_4$ and the applied electrode potential, and for nanotechnological applications a monodisperse size distribution would certainly be advantageous. Nevertheless our studies show for the first time, that Ge nanoclusters with a relatively narrow height distribution can be made by electrochemical means and that these clusters are remarkably stable *in situ* for about one day, even during permanent probing with an STM tip. In contrast to UHV experiments, electrochemistry provides a unique chance to deposit and dissolve Ge clusters reproducibly. In general, it is interesting to study the properties of such clusters as a function of size. Physical parameters of interest are for example the size dependence of band gap and the work functions of the individual nanoclusters. Hitherto most of such studies have been performed under UHV conditions on Ge nanoclusters made by molecular beam or sputtering techniques. In our opinion electrochemical production of such nanoclusters in ionic liquids is an elegant and relatively easy to perform supplement to the well known UHV techniques. Nanoscale electrodeposition studies from ionic liquids are still at their infancy, and we believe that in the near future systems will be available that will allow to make nanoclusters of Si and of less noble compound semiconductors such as *e.g.* GaSb and GaAs.

Fig. 2 Ge nanoclusters with varying heights on Au(111) from the ionic liquid: 1 h after deposition (a), 8 h after deposition (b), 16 h after deposition (c). The *z*-scale is valid for (a)–(c) and the surface was permanently probed with the STM. A height histogram of the clusters is shown in (d) whilst (e) shows typical I/U tunnelling spectra on top of the big clusters that are marked by numbers in (b).

Notes and references

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