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Formation of nanoporous noble metal thin films by electrochemical dealloying of Pt_xSi_{1-x}

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We demonstrate the synthesis of nanoporous Pt thin films on Si by electrochemical dealloying. Amorphous Pt_xSi_{1-x} films (~100–250 nm thick) are formed by electron beam codeposition and dealloyed in aqueous HF solutions at an electrochemical potential sufficient to selectively remove Si while allowing self-assembly of Pt into a nanoporous structure. The Pt nanoporous layers have a pore size of 5–20 nm, ligament thickness ~5 nm, a surface area enhancements >20 times, and an ultrafine grain polycrystalline microstructure. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2161939]

Electrochemical dealloying is a well known process for the selective removal of the most active species from an alloy and the resulting formation of an interconnected porous metal structure. It has been studied for a wide range of corrosion reactions where removal of the more active component occurs under open circuit conditions, e.g., Cu–Zn (brass), Cu–Au.[1] More recently dealloying of bulk metal-metal binary alloys has been studied in detail for the Ag–Au system.[2] The dissolution of the more active species (Ag) from a homogeneous alloy results in the self-assembly of the remaining species (Au) by surface diffusion into a high surface area bicontinuous network with pore sizes as small as 2–3 nm. High surface area catalytic electrode materials play a central role in fuel cells, electrochemical sensors, and hydrogen generation in photocatalytic cells and there is increasing interest in methods to form nanoporous architectures on surfaces, membranes, and in microsystems.[3–6]

Based on the dealloying approach we have developed a method to synthesize nanoporous layers of noble metals (such as Pt and Au) integrated onto silicon substrates. Our synthesis approach is based on the electrochemical dealloying of vapor deposited homogeneous metal silicon films. We demonstrate that dealloying of amorphous Pt_xSi_{1-x} films results in the formation of Pt nanoporous structures with pore sizes between 5 nm and 20 nm. While dealloying has been studied extensively in binary metal alloy systems, there are no reported studies of nanoporous structures formed by dealloying metal silicide systems. This approach enables the integration of a "bottom up" dealloying self-assembly process with "top down" fabrication for Si-based microsystems.

Pt_xSi_{1-x} films of uniform composition with $x \sim 0.2$, 0.35, and 0.5 were deposited at room temperature on *n*-doped Si (100) substrates by coevaporation in a multiple source electron-beam system with a base pressure of 5×10^{-8} Torr. Film thicknesses were varied from 100 to 250 nm. A 1 nm layer of Cr or Ti was deposited just prior to the PtSi film deposition; without this adhesive layer stress-induced delamination occurred during the electrochemical dealloying. Also in most cases a thin (20–40 nm) Pt underlayer was deposited between the adhesive layer and the PtSi film, which served as a convenient electrochemical marker for the end of the dealloying process. The room temperature deposited silicon rich Pt_xSi_{1-x} alloy films are expected to be amorphous and the pure Pt deposited underlayers polycrystalline, and this was confirmed by x-ray diffraction. Rutherford backscattering spectrometry (RBS) with 2 MeV He together with RUMP simulations was used to determine the film compositions and thicknesses. Some oxygen was found to be present in the as-deposited films using He resonance scattering, with the amount quantitatively determined by RBS analysis. The dealloying characteristics of the films were studied using a standard three-electrode cell configuration with an electrolyte of 3% hydrofluoric acid in 18 MΩ distilled and deionized water (Nanopure system). The electrodes consisted of a Pt counter electrode, a saturated calomel reference electrode (SCE), and the deposited Pt_xSi_{1-x} films (~1 cm^2 area) as the working electrode.

The potential sweep vs SCE for a codeposited film containing 21% Pt in Si on top of a thin Pt underlayer is shown in comparison to that for pure Si in Fig. 1. The clear change in morphology from an initially smooth to a highly porous surface after the potential sweep indicates the formation of the nanoporous structure with observed pore sizes ranging between ~5 nm and 20 nm and Pt ligament widths of ~5 nm. The increase in current density in Fig. 1 near 0.2 V

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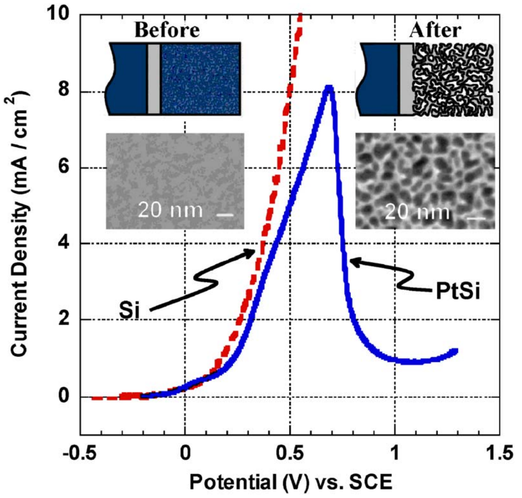

FIG. 1. Linear potential sweeps at 10 mV/s for pure silicon and for a 130 nm $Pt_{0.21}Si_{0.70}O_{0.09}$ film with a 20 nm Pt underlayer on Si. Insets show schematic cross sections and plan-view SEMs of the as-deposited (left side) and dealloyed (right side) samples.

is thus inferred to be due to the dealloying of Si ions from the PtSi alloy and is consistent with the rapid increase in Si dissolution for a bulk Si (100) surface. The subsequent drop in current density for the PtSi film above 0.7 V is attributed to exhausting the Si from the PtSi alloy. Similar dealloying results were obtained for four different Pt_xSi_{1-x} codeposited films with a Pt composition between $x=0.18$ and 0.21 and thicknesses between 100 and 250 nm. The oxygen background concentrations ranged from 2 to 9 at.%, in these films, suggesting these levels of O do not critically affect the dealloying process. The critical potential for dealloying ($\sim$0.2 V in Fig. 1) is a rate dependent parameter which decreases as sweep rate is increased. Based on our conditions the subsequent film dealloying studies were carried out at a constant potential of 0.6–0.8 V.

In addition to SEM analysis, depth dependent compositional analysis was performed by RBS before and after dealloying to verify the removal of Si. Figure 2 contains spectra for two different samples containing 20% Pt with and without an underlying pure Pt barrier layer. The RBS spectra verify complete removal of silicon atoms from the Pt_xSi_{1-x} alloys while retaining all the Pt atoms in the original films.

The structure of a dealloyed nanoporous Pt film was studied in more detail using field-emission transmission electron microscopy (JEOL 2010F). In Fig. 3(a) the light regions of the Z-contrast scanning transmission electron micrograph (STEM) indicate a well defined bicontinuous “honeycomb” structure with areas of high and low density conforming to irregularly shaped pore sizes of 10–25 nm. The ligaments connecting the pores in Fig. 3(a) have a width of about 5–7 nm. Electron energy-loss spectroscopy (EELS) verified the presence of Pt for the nanoporous structure from the Pt 3d ionization edge at 2122 eV [Fig. 3(a) inset], as well as no detectable Si at 1839 eV. Both high resolution transmission electron microscopy (HREM) and selected area electron diffraction [Fig. 3(b) and inset] indicate the nanoporous connecting ligament microstructure is composed of fine-grained, randomly oriented fcc polycrystalline Pt with an average nanocrystalline grain size of 3–5 nm. We note that for nanoporous structures with about 5 nm wide ligaments the fraction of atoms at a surface in the structure approaches 10%.

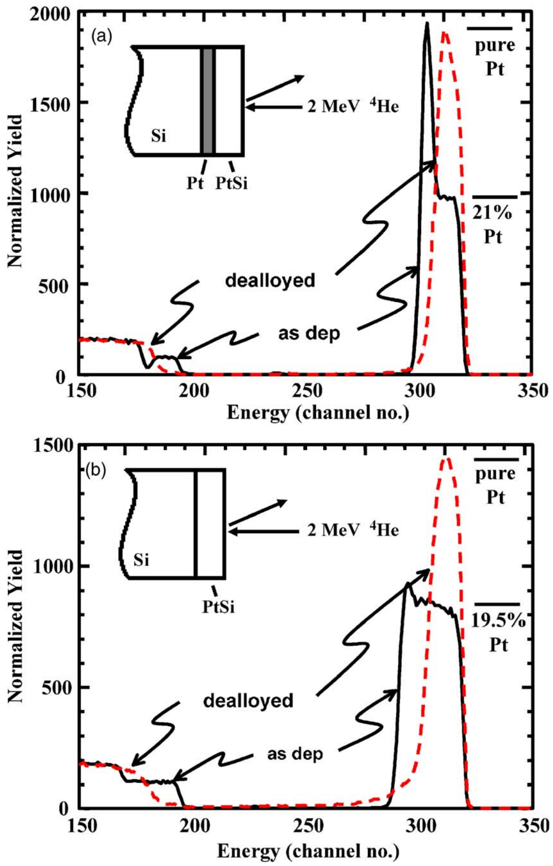

FIG. 2. RBS spectra using 2 MeV He for PtSi thin film samples as deposited and after dealloying for (a) $Pt_{0.21}Si_{0.70}O_{0.09}$ film with underlying 20 nm Pt barrier layer (same deposition as for Fig. 1), and (b) $Pt_{0.20}Si_{0.75}O_{0.05}$ with no Pt barrier layer. Backscattering level near channel 300 for pure Pt (as indicated by horizontal line in upper right corner) corresponds to the scattering level for pure Pt and is consistent with the observed level after dealloying, indicating the complete removal of Si (and O) atoms by dealloying.

Dealloying was also investigated for Pt_xSi_{1-x} codeposited films with higher Pt concentrations corresponding to $x=0.35$ and 0.5. In addition polycrystalline PtSi films were formed by Pt deposition and annealing to form the most Si rich silicide phase, PtSi. It was found that for $x=0.35$ the Si dissolution and nanoporous Pt film formation occurred with the average pore sizes somewhat larger than for $x\sim0.2$. However, for $x=0.5$ dealloying was not observed for either the codeposited amorphous or the polycrystalline PtSi silicide films, consistent with the typically 15%–40% concentrations required for the more noble species in binary metallic alloys for dealloying to occur.

The dealloyed nanoporous Pt films were heated in a flowing inert gas atmosphere tube furnace for 10 min at 800, 850, and 900 °C. As shown in Fig. 4, SEM micrographs of the surface morphology show a pore size increasing with anneal temperature from approximately 10 nm to 40 nm at the highest anneal temperature. At these temperatures, which correspond to homologous temperatures of 0.52 to 0.57, surface diffusion is expected to become appreciable, thus enabling the observed coarsening.

Since the formation of nanoporous structures have, to our knowledge, not been reported previously for noble metal-silicon alloys,[7] it is illustrative to compare this system to the characteristics typically possessed by binary alloys that form nanoporous structures by dealloying.[1,2,8] First, one species is typically more noble than the other by several

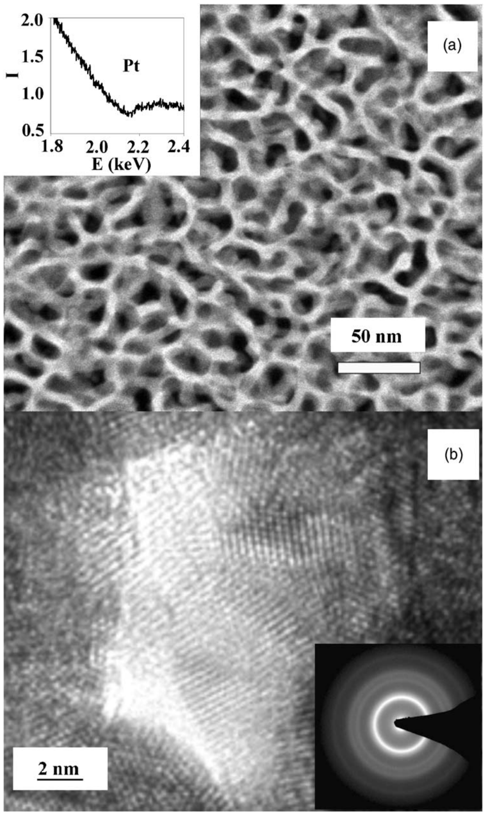

FIG. 3. (a) Z-contrast STEM image after dealloying for the Pt nanoporous structure revealing pores sizes on order of 10–25 nm (the lighter areas correspond to the nanoporous Pt ligaments). The sample was prepared by floating the nanoporous film in the electrolyte onto a Cu grid after dealloying for a Si substrate without a Cr adhesive layer. Insert shows the electron energy-loss spectrum near the Pt M_{45} edge. (b) HREM showing randomly oriented nanoscale grains with lattice fringes corresponding to the (111) and (200) plane spacing of Pt metal. Insert shows selected area electron diffraction pattern which indexes to Pt metal.

hundred millivolts such that the less noble species is electrochemically extracted upon dealloying at an intermediate potential, and this is the case for our Pt_xSi_{1-x} system. Second, the composition is usually richer in the less noble species and this is consistent with our observations of dealloying for 20 and 35 at. % Pt in Si, but not for 50% Pt. Third, in order for a homogenous dealloyed microstructure to evolve, the alloy must be single phase. Our method of codeposition of metal-silicon films near room temperature enables the ready formation of homogeneous single phase alloys, which in most cases are expected to be amorphous, and we note that the dealloying process proceeds in our amorphous PtSi alloys similar to that for the previously studied crystalline binary metallic systems.[1–6,8]

The increase in surface area for the Pt nanoporous films was measured by Cu underpotential deposition (UPD). At potentials slightly higher than the thermodynamically reversible potential UPD can results in the deposition of a single pseudomorphic Cu monolayer onto polycrystalline Pt surfaces.[9] The nanoporous Pt was swept and held at the potential where one full Cu monolayer forms for an extended time to allow Cu ions to diffuse into the porous structure and then swept back to strip the Cu^{2+} ions at a slow sweep rate (1 mV/s) to measure the deposited Cu monolayer which is directly proportional to the electrode surface area. A 22-fold increase in surface area was obtained for dealloyed films of 130 nm thickness, which corresponds to 41 m^2/gm for these nanoporous films, a value comparable to that for Pt black catalysts. This UDP determined surface area is also consistent with simple geometric estimates based on our measured mean pore size, surface density, and film thickness for the nanoporous layers.

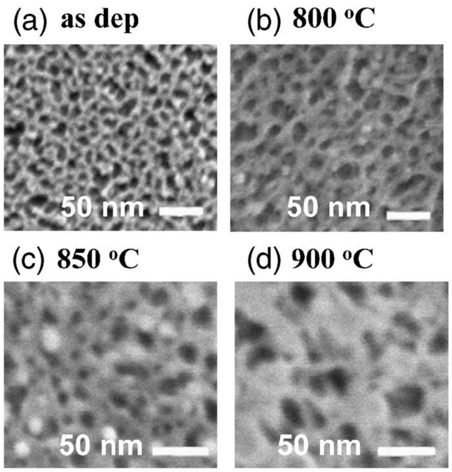

FIG. 4. SEM images of the dealloyed Pt surface (a) as-deposited, and after 10 min anneals at (b) 800 °C, (c) 850 °C, and (d) 900 °C showing an increase in pore size due to coarsening with increasing temperature.

To explore the catalytic reactivity of these nanoporous Pt electrodes preliminary measurements were carried out for hydrogen production in a photoelectrochemical cell.[10] The Pt electrode served as the cathode of a hybrid cell that couples a dye-sensitized nanoparticulate wide band gap semiconductor photoanode to the enzyme-based oxidation of glucose at the cathode. For the nanoporous Pt electrode the hydrogen production rate, while below that observed for commercial Pt impregnated fuel cell electrodes, was found to be increased a factor of 10 over that for a smooth Pt foil electrode.

In summary electrochemical dealloying of amorphous platinum-silicon codeposited alloys results in the self-assembly of ultrafine grain polycrystalline nanoporous noble metal structures, providing a new approach to forming high surface area electrodes on Si for emerging applications such as microfuel cells, biosensors, microbatteries, and supercapacitors.

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