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XAFS studies of Rh nanostructures on porous silicon

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Rh $L_{3,2}$-edge and Si K-edge X-ray Absorption Near Edge Structure (XANES), and X-ray excited optical luminescence (XEOL), have been used to characterize the electronic structure of Rh nanoclusters deposited on porous silicon and the effect of Rh deposition on the optical properties of porous silicon.

Keywords: Rh nanostructure, porous silicon, XEOL, XANES

1. Introduction

Porous silicon (PS), a sponge-like crystalline Si known to emit visible light at room temperature, is a candidate for optoelectronic applications (Cullis et al. 1997). However, luminescence efficiency, mechanical stability and transport properties of porous silicon are the main concerns if porous silicon is to be used in a microelectronic device.

Deposition of metals from a liquid phase is an effective and low cost method to fill the porous film with a conductive solid. This process may improve the mechanical stability and the electrical transport property of PS. We have developed a technique in which metals are deposited from solution onto the internal surface of porous silicon. This process takes advantage of the modest reducing power of porous silicon (Coulthard et al. 1993; Sham et al. 1994; Coulthard & Sham 1997; Jiang et al. 1993). We show here with Rh $L_{3,2}$-edge and Si K-edge XANES that Rh nanostructures are formed on PS, that the presence of Rh inhibits the oxidation of PS layers and that Rh deposition suppress but does not quench completely the luminescence from the PS substrate.

2. Experimental

Porous silicon samples were prepared using an electrochemical cell with the silicon wafer acting as the anode and a Pt foil as the counter electrode (Coulthard et al. 1993) The porous silicon film was left attached to the substrate. The thickness of the PS film is typically several to tens of μm. The thickness and porosity of the film generally increase with current density and time of etching (typical preparation condition: 20 mA/cm^2, 20 min). Rh was deposited onto the porous silicon film (~1 cm^2 surface area) at room temperature from an aqueous solution of $Na_3[RhCl_6]$ (1 x 10^{-4} M, 10 min). The substrate was "refreshed" with HF prior to deposition.

We characterized the morphology and crystal structure of the Rh deposits with Scanning Electron Microscopy (SEM) and X-Ray Powder Diffraction (XRD). X-ray absorption near-edge structure (XANES) were obtained at the Double Crystal Monochromater beamline (InSb (111) crystals) of the Canadian Synchrotron Radiation Facilities (CSRF) at the Synchrotron Radiation Center (SRC), University of Wisconsin-Madison. X-ray excited optical luminescence (XEOL) was recorded with a J-Y H10 monochromator equipped with a Hamamatsu R943-02 photomultiplier tube. XANES were recorded in total electron yield (TEY) and sometimes photoluminescence yield (PLY).

3. Results and Discussion

The XRD of Rh/PS shows that the Rh deposit on porous silicon is fcc rhodium. The broadening of the Rh <111> diffraction peak shows the presence of very small Rh crystallites (~5 nm on average). SEM shows a uniform film on the PS surface. High magnification reveals a distribution of aggregates varying in size from nm to tens of nm. The cross-section image of the specimen clearly reveals that the PS channels were filled with Rh beyond ~ 2 μm below the nominal surface. The presence of Rh is also confirmed with Energy Dispersive X-ray fluorescence (EDX).

Fig.1 shows the Rh $L_{3,2}$ edge XANES (TEY) of Rh metal and two Rh/PS samples of which the substrates were prepared with modest and high current density for 20 min. We see that while the XANES for the 20 mA/cm^2 sample is noisy and lack of well-defined features in the higher photon energy region, the thicker and more porous 60 mA/cm^2 sample clearly exhibits XANES characteristic of Rh metal except for broadened features (a sign of disorder due to increasing surface to bulk atom ratio in small crystals). Close examination shows that the L_3 whiteline for the high current density sample is more intense than the metal as judged by a positive area under the difference curve between the whiteline of the Rh/PS sample and Rh metal (more details will be published elsewhere). The L_2-edge is less reliable here due to a high background and possible sample uniformity problem in the PS sample. The whiteline intensity indicates that relative to Rh metal, Rh on PS loses d charge, not an unexpected result as the number of like-nearest neighbors decreases in small nanocrystallites (Coulthard et al. 1993).

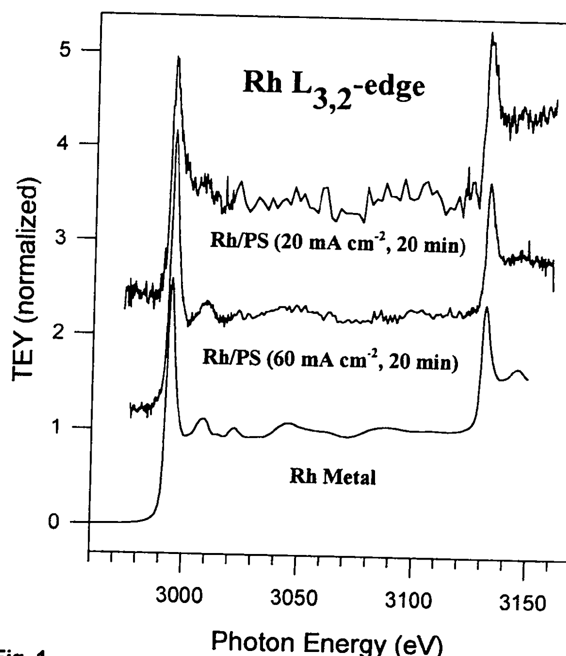

Fig. 1
Rh $L_{3,2}$-edge XANES of Rh metal and two Rh/PS samples (10 min deposition).

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Fig. 2 compares the Si K-edge XANES of a PS (20mA/cm^2, 20 min) before and after Rh deposition as well as an ambient and HF refreshed Si (100). The Si K-edge XANES are typical of those reported previously (Sham et al. 1993) and exhibit a whiteline at ~ 1840 eV followed by two peaks at 1844 and 1847 eV. The three-peak pattern in ambient PS has been attributed to Si-Si, Si-H/Si-OH/sub-oxide and SiO_2 bonding, respectively (Coulthard et al. 1993; Coulthard & Sham 1997). From the relative intensity of the PS and the oxide peak (marked with vertical bars), we infer that Rh deposition suppress the oxidation of PS in the ambient.

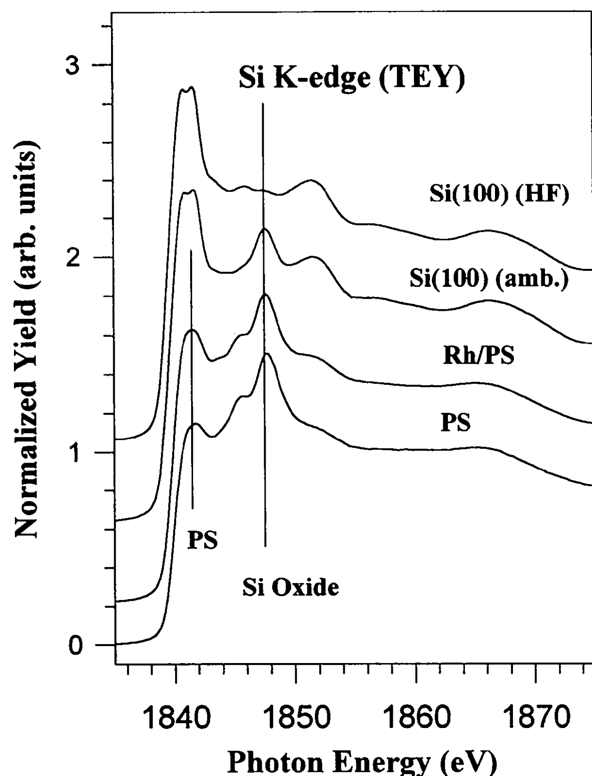

Figure 2
Si K-edge XANES of PS before and after Rh deposition and an ambient Si(100) before and after HF refresh. The positions of the PS and SiO_2 resonances are marked.

Fig. 3 shows the XEOL of a PS sample before and after Rh deposition (excitation energy = 1840 eV). We see that the luminescence pattern remains essentially the same, only the intensity is reduced (to ~30%). Fig.4 shows the PLY XANES of a series of Rh/PS samples prepared at a constant current density of 20 mA/cm^2 and increasing anodization times (from 5 to 30 min), therefore an increase in sample thickness. The optical XANES exhibits a trend similar to those reported previously for PS (Sham et al. 1993; Coulthard & Sham 1997). Thus Rh deposition does not appear to affect the luminescence pattern other than a reduction in intensity. This observation confirms that luminescence from PS arises from quantum confined nanosize crystallites and Rh deposition does not significantly alter the origin of the luminescence. The presence of the metal, however, will compete for photons and facilitate non-radiative recombination of holes and electrons, reducing the quantum efficiency.

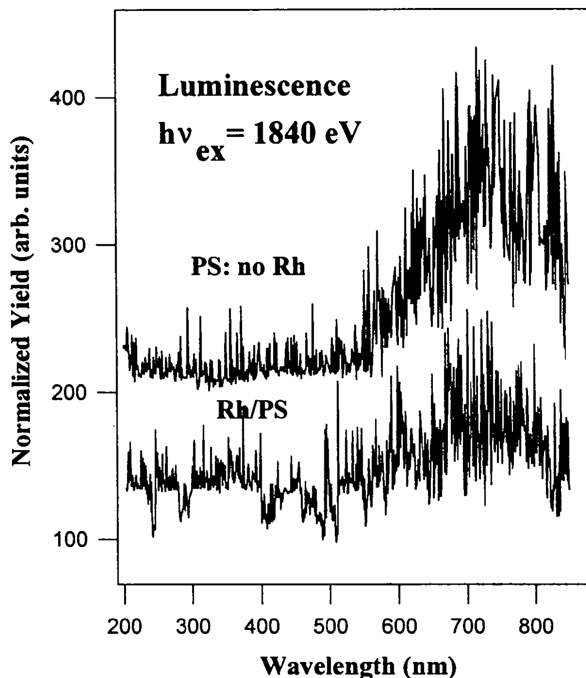

Figure 3
Luminescence from PS before and after Rh deposition; the PS spectrum has been shiftedvertically for clarity.

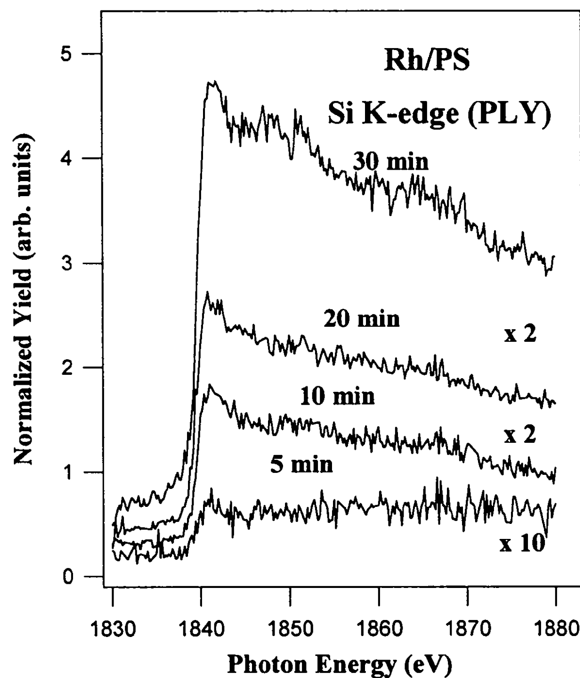

Figure 4
PLY XANES for a series Rh/PS samples; current density used in PS preparation in noted.

4. Conclusions

X-ray results show that controlled reductive deposition of Rh metal nanostructures from an aqueous solution onto porous silicon has been realized. XEOL and optical XANES of Rh/PS samples show similar features as their substrate before deposition although with some reduction in PLY. This suggests that the mechanism of luminescence is not altered drastically by Rh deposition.

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