

A PHOTOEMISSION STUDY OF ELECTROCHEMICALLY ETCHED LIGHT EMITTING SILICON

JEFF TERRY,^a H. LIU,^b R. CAO,^a J. C. WOICIK,^c P. PIANETTA,^a X. YANG,^a J. WU,^a M. RICHTER,^a N. MALUF,^b F. PEASE,^b A. DILLON,^d M. ROBINSON,^d and S. GEORGED

^aStanford Synchrotron Radiation Laboratory, Stanford, CA 94309

^bStanford Electronics Laboratories, Stanford, CA 94309

^cNational Institute of Standards and Technology, Gaithersburg, MD

^dDepartment of Chemistry, University of Colorado, Boulder, CO

ABSTRACT

The valence band and the Si 2p core level of electrochemically etched light emitting porous silicon samples prepared with different etching parameters and upon thermal annealing have been studied. The core level shows appreciable broadening as chemical etching time increases. Upon annealing, the core level linewidth decreases and the valence band develops spectral features. The photoluminescence intensity, also, decreases upon annealing. However, impurity species are found to be present only in trace amounts. Our data is consistent with a photoluminescence mechanism involving a silicon species that degrades, decomposes, or desorbs upon annealing.

INTRODUCTION

Recently, it has been shown that silicon could be made to show appreciable luminescence above the band gap under optical excitation[1]. This discovery may allow the production of silicon based optoelectronic devices which are more desirable than present technology because of the widely developed Si device technology. However, it will not be possible to utilize light emitting porous silicon in optoelectronic devices until the luminescence mechanism is understood. The photoluminescence has been observed from silicon that has undergone electrochemical dissolution[1] and anodic oxidation[2]. The anodization forms a porous layer with the pores propagating in [100] directions[3]. It has been postulated that when the pores become large the small unetched portions act as quantum wires[1]. Complicating the analysis, photoluminescence has also been observed from microcrystalline Si particles[4] and from silicon subjected to a stain etch[5], which supposedly has structure similar to that of porous Si[5]. Many theories have been proposed to account for the photoluminescence: quantum confinement[1], amorphous Si emission[5,6], SiH₂ on the surface acting as recombination centers[7], and the presence of a high concentration of a luminescent species on the large surface area of the porous layers[8]. Recently, using surface sensitive EXAFS spectroscopy, we have shown that the surface of electrochemically etched porous silicon is crystalline[11]. Because the silicon is not amorphous, a luminescence mechanism based on amorphous silicon is not possible. In order to gain a better understanding of the mechanism of the luminescence we have used high-resolution core level spectroscopy and valence band spectroscopy to study the electronic structure of porous silicon formed by electrochemical dissolution and chemical etching similar to those of Canham[1].

EXPERIMENTAL

The photoemission experiments were performed on Beam line III-1, Beam line I-2, and Beam line III-3 at the Stanford Synchrotron Radiation Laboratory (SSRL). Beam line III-1 uses a Grasshopper monochromator that allowed study up to the C 1s core level. Higher photon energies from this monochromator did not have adequate flux to investigate higher binding energy core levels. The vacuum chamber consists of a sample load lock, a prep chamber, and an analysis chamber. The analysis chamber houses a double pass cylindrical mirror analyzer. The overall instrumental resolution (monochromator and spectrometer) for the photoemission experiment was about 0.3 eV at a photon energy of 150 eV. Beam line I-2