

Potentiostatic Preparation of Porous Silicon

Chi-Woo Lee*, Dong-Ill Kim, and Mi-Kyung Oh

Department of Chemistry, College of Natural Sciences,
Korea University, Choongnam 339

Received September 30, 1992

Since electrochemically and chemically etched silicon or porous silicon was reported to be luminescent¹, stupendous research efforts were driven to understand the origin and mechanism of the strong visible luminescence and to fabricate possible optoelectronic devices based on porous silicon²⁻⁷. Experimental evidences have shown that quantum confinement effects on band structure of silicon were to cause porous silicon to emit visible light under ultraviolet illumination²⁻⁵, while a recent work described a chemical mechanism on the visible light emission from porous silicon⁶. To observe quantum size effects the characteristic widths of Si skeletons need to be significantly less than the dimensions of the free exciton (~ 50 Å) of bulk Si. A suitable etching method is the one that will enlarge each pore at an extremely slow but controllable rate and will leave a chemically passivated surface¹. Constant potential methods will be preferred for the purpose to constant current ones, because the former offer better selectivity, current efficiency and control when the sufficient experimental conditions are found. All previous electrochemical procedures of producing porous silicon, however, involved a constant current or galvanostatic mode. In this work we describe for the first time that a constant potential or potentiostatic mode is applicable to fashion porous silicon. In addition the surface of luminescent porous silicon thus prepared is described to be modified by self-assembled octadecyl mercaptan.

Luminescent porous silicon samples were prepared by potentiostatically etching *n*-Si (P-doped, 1.0-2.0 Ω cm resistivity, (100) orientation) in a solution of hydrofluoric acid and ethanol (1:1) at 1-3 V versus platinum quasireference electrode under UV irradiation (Spectronic Co. Model ENF-240C) for 20 min. The samples were dried in the air and transferred to the chamber of octadecyl mercaptan, which was heated at 80°C for one day to form self-assembled octadecyl mercaptan on porous silicon. Electrochemical experiments were per-

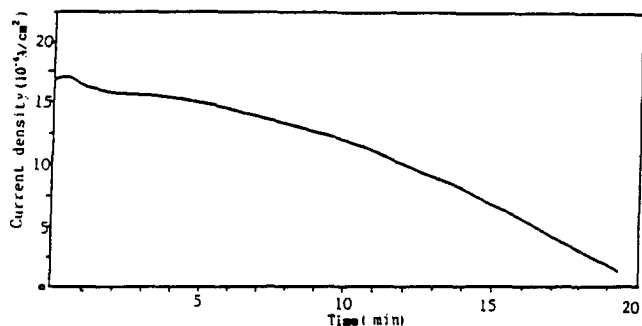


Figure 1. Chronoamperometric curve obtained with steady P-doped Si (100) immersed in ethanolic solution of hydrofluoric acid (1:1) under UV illumination at 1.5 V versus platinum quasireference electrode.

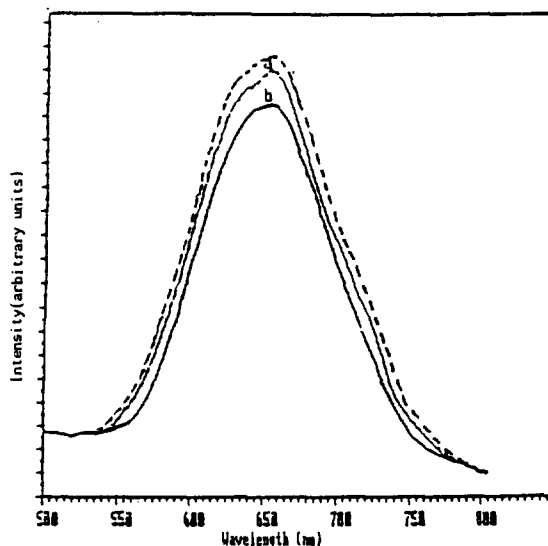


Figure 2. Emission spectra of porous Si prepared potentiostatically (full lines) with (a) and without (b) self-assembled octadecyl mercaptan and galvanostatically (dotted line). $\lambda_{\text{ex}} = 365$ nm.

formed in a two-compartment cell using an EG & G PAR Versastat interfaced to Discorp 386 personal computer. The photoluminescence of the porous Si samples was measured using HITACHI 650-60 Fluorescence Spectrophotometer.

Figure 1 shows a chronoamperometric curve observed with a steady *n*-type Si (100) in an ethanolic solution of hydrofluoric acid, where the current decay is not a Cottrell type, indicating that electrochemical oxidation takes place within the Si wafer. Red luminescence of the porous silicon dried was visible to the naked eye under unfocused 1 mW blue excitation in the laboratory. Figure 2 shows the emission spectra of porous silicon with and without surface film of self-assembled octadecyl mercaptan. The luminescence of surface-protected porous Si was slightly lower in its intensity but lasted longer (months). A drop of water on the octadecyl mercaptan-covered porous silicon did not generate any gas, while the same experiments with porous silicon generate unidentified gases. A contact angle of water drop on the protected silicon was larger than the one on the unprotected one. Thus reactive⁹ or surface-sensitive¹⁰ porous silicon surfaces appear to be protected by octadecyl mercaptan film. Shown also in Figure 2 is an emission spectrum of porous Si prepared galvanostatically at 5 mA/cm² for 30 min and 50 mA/cm² for 25 sec. The spectra are very similar and the luminescent properties of porous silicon samples appear to be identical in both cases of the galvanostatic and potentiostatic preparation.

In summary, light-emitting porous silicon was prepared potentiostatically and the protection of the porous surface was accomplished by self-assembled octadecyl mercaptan. The potentiostatic procedure of preparing porous Si is expected to facilitate the investigation of the origin of light production and the fabrication of optoelectronic devices based on porous Si. Further studies on porous Si prepared potentiostatically are in progress in this laboratory.

Acknowledgement. This work was supported by Korea Science and Engineering Foundation and the Ministry of Education. We thank S. Y. Lee for his assistance. We also

thank Prof. N. Min of the Department of Control and Instrumentation Engineering of Korea University and Dr. D. Oh of Electronics and Telecommunications Research Institute for generous donation of Si wafers.

References

1. L. T. Canham, *Appl. Phys. Lett.*, **57**, 1046 (1990); C. Pickering *et al.*, *J. Phys. C.*, **17**, 6535 (1984).
2. L. T. Canham, M. R. Houlton, W. Y. Leong, C. Pickering, and J. M. Keen, *J. Appl. Phys.*, **70**, 422 (1991).
3. K. A. Littau, A. Mulle, P. J. Szajowski, and L. E. Brus, "Extended abstracts of the 182nd Electrochemical Society Meeting", Toronto, Canada, 825 (1992).
4. A. Nakajima, T. Hakura, Satoru Watanabe, Y. Sugita, Y. Nara, and N. Nakayama, "Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials", Tsukuba, Japan, 472 (1992).
5. T. V. Buuren, Y. Gae, T-Tiedje, J. R. Dahn, and B. M. Way, *Appl. Phys. Lett.*, **60**, 3013 (1992).
6. P. McCord, S.-L. Yau, and A. J. Bard, *Science*, **257**, 68 (1992).
7. V. V. Doan and M. J. Sailor, *Science*, **256**, 1791 (1992).
8. C. W. Sheen, J.-X. Shi, Jan Martensson, A. N. Parikh, and D. L. Allara, *J. Am. Chem. Soc.*, **114**, 1514 (1992).
9. T. Unagami and M. Seki, *J. Electrochem. Soc.*, **125**, 1339 (1978).
10. J. M. Lauehaas, G. M. Credo, J. L. Heinrich, and M. J. Sailor, *J. Am. Chem. Soc.*, **114**, 1911 (1992).
11. D.-I. Kim, M.-K. Oh, and C.-W. Lee, unpublished results.

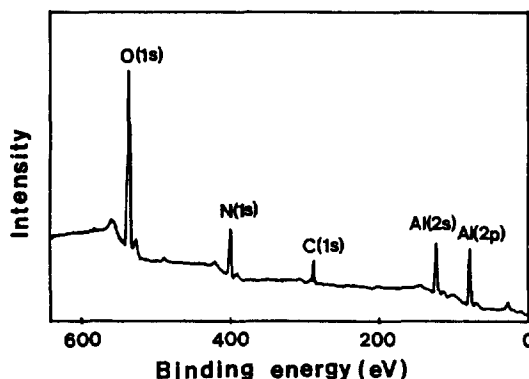


Figure 1. XPS spectrum of Film II deposited at 500°C.

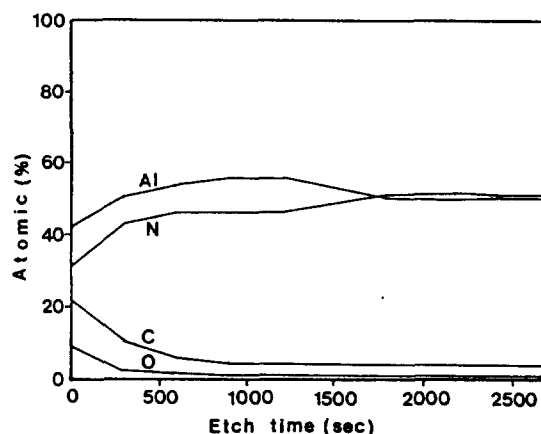


Figure 2. Auger depth profile of Film II deposited at 500°C.

Preparation of Aluminum Nitride Thin Films Using Single Precursor OMCVD

Joon T. Park*, June-Key Lee, Sehun Kim,
Myung Mo Sung†, and Yunsoo Kim†

*Department of Chemistry,
Korea Advanced Institute of Science and Technology,
Taejeon 305-701

†Advanced Materials Division,
Korea Research Institute of Chemical Technology,
Taejeon 305-606

Received October 12, 1992

The preparation of aluminum nitride (AlN) thin films has received much attention due to its potential applications in the electronic and optoelectronic devices.¹ AlN has the wurtzite crystal structure, a large band gap of about 6.2 eV, a high decomposition temperature (*ca.* 2400°C), and good chemical stability. It is a promising material for electronic substrates such as passivation and dielectric layers, protective coatings, surface acoustic wave devices, and optical devices.¹ Several techniques have been employed for the preparation of AlN thin films including conventional organometallic chemical vapor deposition (OMCVD),² molecular beam epitaxy (MBE),³ and single precursor OMCVD.⁴ The single precursor

OMCVD has been shown to have a number of important advantages over the conventional CVD processes.⁵ Several groups^{4,6} recently reported the preparation of group III-V semiconductor films using the single precursor OMCVD method, especially, at low temperatures ($\leq 500^\circ\text{C}$) in order to be compatible with current semiconductor device technology and to prevent interdiffusion of layers. In this communication we report the preparation and characterization of AlN thin films by single precursor OMCVD with two amidoalane dimers, $[\text{Me}_2\text{Al}(\mu\text{-NHA'Bu})_2]_2$ (**1**) and $[\text{Et}_2\text{Al}(\mu\text{-NH'Bu})_2]_2$ (**2**).

The single precursors, **1**⁷ and **2**,⁸ were prepared and purified by sublimation as previously described. Film growth conditions involved the use of a hot-wall CVD apparatus. Silicon (100) wafers ($10 \times 10 \text{ mm}^2$) were used as substrates.⁹ The base and the steady state pressures of the CVD reactor were $(3\text{--}5) \times 10^{-5}$ and $(1\text{--}2) \times 10^{-4}$ Torr, respectively. AlN films were grown in the temperature range 200–800°C with both precursors. The optimum temperatures for the film growth with precursors **1** and **2** were found to be 650°C (Film I) and 500°C (Film II), respectively.¹⁰ Atomic compositions of the films were determined by X-ray photoelectron spectroscopy (XPS) and a typical XPS spectrum of the AlN film (Film II) is shown in Figure 1. The respective Al 2s, Al 2p, N 1s, C 1s, and O 1s peaks at 120.5, 74.0, 396.7, 285.0, and 531.7 eV¹¹ reveal the Films I and II to have comparable amounts of Al and N with surface contamination of carbon and oxygen.¹² Auger depth profile studies were performed using argon ion sputtering in which the Al, N, C, and O