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Title : Surface Stability Studies of Porous Silicon by Vibrational (Raman or IR) Spectroscopy

ABSTRACT

Silicon (Si) is most dominating material in microelectronic industry due to its ideal band-gap (1.12 eV) for room temperature operation, low temperature sensitivity, ease of processibility and ease of availability. However, considering its indirect band gap nature, Si is an inefficient light emitter. In addition, competitive non-radiative recombination rates are much higher in standard bulk Si than the radiative ones and most of the excited e-h pairs recombine non-radiatively resulting in yield of very low internal quantum efficiency.

It was found by Canham that when silicon was made nanoporous, its luminescence efficiency was greatly enhanced and photoluminescence obtained in visible range at room temperature. Since the discovery of visible luminescence from porous silicon, a strong interest and hype was generated among the researchers for its enormous potential applications in the field of microelectronics, sensors, biochemistry and optoelectronics. Somehow, the interest on porous silicon has been waned away mainly because of its surface instability as no long term device can be made where surface degradation changes the device characteristics with time. The degradation even starts immediately after the exposure to ambient air. This compelled the researchers to look into this fundamental problem with a view to arrest the cause by evolving new concept and technology.

Numerous treatments to stabilize porous silicon structure have been reported like chemical treatment, carbonization, thermal treatment and photo-induced electrochemical anodization method; but till date no method have shown any long term surface stability of porous silicon.

This thesis summarizes a three years scientific research investigation on the design and fabrication of porous silicon and further surface stability techniques of porous silicon. Porous

silicon is an ideal material for sensing applications due to its sponge-like morphology, characterized by a specific surface area up to $500 \text{ m}^2 \text{ cm}^{-3}$, which assures an effective interaction with gas and liquid substances. Moreover, porous silicon is a low cost material, completely compatible with standard microelectronic processes.

In the present thesis, the porous silicon surface has been modified in order to gain chemical stability. The PS samples were then investigated through scanning electron microscope (SEM), micro-Raman, Photoluminescence (PL), Energy-dispersive X-ray spectroscopy (EDS) and Fourier Transform Infrared (FTIR) spectroscopy.

In literature various methods of fabrication of PS are mentioned like stain etching, electrochemical anodization, laser induced etching (LIE), reactive ion etching, lithography etc. However electrochemical anodization is adapted for our sample fabrication considering simplicity, cost effectiveness and quality of the sample produced by this method.

SEM is used to study the surface morphology of our PS samples in detail. Electron beam in very high magnification is used for observing SEM results. The reduced dimensionality of PS could lead to confinement of electron and phonons which could subsequently result in major modification in its optical and vibrational properties in comparison to that of bulk. In this work, photoluminescence, Raman spectroscopy and FTIR spectroscopy techniques were used to study modification of optical and vibrational properties of PS by variation in etching parameter.

When PS sample left in ambient for ageing, its photoluminescent properties are affected considerably. Hence, PL is also affected considerably. Remarkable blueshift and variations in the luminescence maximum observed when PS samples stored in the air for several days. This instability in PL spectrum could hinder its possible applications in various areas. Several authors have suggested that in addition to confinement of electrons, surface nature of PS also play an important role in origin and modification of photoluminescence.