ABSTRACT

Key words: *porous silicon, electrochemical anodisation, front surface anodisation, electrolyte, isopropanol, constant current density, UV-illumination, photoluminescence, electroluminescence, PL spectrum, EL spectrum, post-anodisation treatment, hydrogen peroxide, red shift, blue shift, peak wavelength, oxygenation, quantum confinement, Si-SiO_2 interface, bandgap widening, micron-size PS patterns, selective anodisation, selectively doped substrates, photoresist-on-oxide mask, low-temperature oxidation, step height, refractive index, isolation, leakage current, breakdown voltage, ECL gate.*

The present thesis deals with systematic experimental studies on the preparation and characterisation of porous silicon (PS) films with improved features for optoelectronic and microelectronic applications.

A brief review of porous silicon films with regard to the mechanism of formation, the techniques of preparation and characterisations has been made. Experiments are conducted to anodise silicon substrates (P-type, N-type and diffused) to form PS films in three different electrolytes, viz., 1:1 vol. of HF:DI water, HF:ethanol and HF:isopropanol solutions at different constant current densities for various times with external UV-illumination for N-type substrates/layers only. Porosity, crystal structure (TEM), surface microstructure (optical microscope, SEM & AFM), composition (XPS) of PS films have been characterised. The AFM and optical microscopy clearly establish that HF:isopropanol electrolyte produces the smoothest surface with less macroscopic etch pits compared to ethanol- and water-based electrolytes.

Photoluminescence (PL) and electroluminescence (EL) spectra of PS films formed on P-type and N-type silicon substrates of doping concentration around $10^{15}/cm^3$ and N-diffused layer into P-type substrate (N-P junction) with a high surface doping concentration ($1.5\times10^{20}/cm^3$) in three different electrolytes, as mentioned above, at constant current density of 30 mA/cm^2 for 5 minutes have been studied. The use of isopropanol has yielded the strongest and the most uniform luminescence and maximum blue shift of peak wavelength. Of the different substrates for anodisation, the N-diffused layer with high surface doping concentration has produced the most intense PL with the maximum negative shift of peak wavelength. The EL obtained from Au (200 Å)-N type porous silicon Schottky junction is similar in nature with PL. Al (200 Å)-N type PS junction emits feeble yellowish-white light over a broad range of wavelengths for a reverse bias in the avalanche region. A similar result is obtained involving emission of feeble reddish-white light from Au (200 Å)-P type PS junction under strong reverse bias only.

The effect of boiling H_2O_2 and UV-irradiated H_2O_2 treatments on PL characteristics of PS films has been investigated in detail. The boiling H_2O_2 treatment for 45 min increases the PL peak intensity by about 700 times and causes a small red shift of the PL peak wavelength by about 20 nm compared to as-anodised sample. The UV-irradiated hydrogen peroxide treatment for 1 hour increases the PL peak intensity by

about 390 times and results in a red shift of the PL peak wavelength by about 60 nm compared to as-anodised sample. In both cases, the large improvement in PL intensity has been predicted to be due to quantum confinement in ultra-small silicon nanocrystallites or quantum boxes and the reduction of nonradiative surface recombination in the pore walls due to oxide passivation. The red shift of the peak wavelength is explained considering the oxygenation of the Si-SiO_2 interface and the formation of local density of states (LDOS) in the bandgap of nanocrystallites.

The author has conducted a detailed experimental study on the formation of micron-size photoluminescent PS patterns by selective anodisation through different masks (photoresist mask, silicon dioxide mask and photoresist-on-oxide mask) and on selectively doped wafers prepared by thermal diffusion of dopants through oxide mask. The techniques do not require a sophisticated equipment like an ion implanter or milling unit. Selective doping with the same type of dopants (N^+-N or P^+-P) can be used for selective anodisation to form PS patterns but the pattern resolution and contrast are limited by the relative resistances to current flow offered by the diffused and nondiffused regions. Very high-resolution and high-contrast photoluminescent PS patterns can be obtained using substrates doped selectively with opposite-polarity dopants (N^+-P or P^+-N). The method has yielded 4 μm resolution patterns with strong photoluminescence.

A systematic study of low-temperature oxidation of porous silicon by furnace oxidation at temperatures of 700°C-900°C in dry and cyclic (dry-wet-dry) oxidation environments and also by treatment in boiling H_2O_2 for various times has been carried out. The resistivity, refractive index, volume expansion (in terms of step height) and other characteristics (XRD & XPS) have been measured for PS films oxidised at different oxidation conditions. The oxidation at 750°C for 5 min dry-30 min wet-5 min dry treatments has produced PS oxide of resistivity 4.5×10^{13} Ω-cm, refractive index 1.34 and volume expansion less than 5%, which is most suitable for isoplanar local oxide isolation (LOCOS) with negligible impurity redistribution. The technique has been applied successfully to the electrical isolation in a 4 μm ECL gate fabrication process using an N-type epitaxial layer of thickness 5.2 μm on a P-type substrate. The leakage current and breakdown voltage between two adjacent epi tubs (120 μm×120 μm) are obtained as 20 - 30 pA and 160 V respectively which are far superior to those achievable with standard junction isolation. The capacitance between the tubs decrease considerably due to the reduction of the side-wall component of capacitance.