Porous Silicon

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Abstract

The discovery that highly porous silicon(PS) obtained by electrochemically etching a silicon wafer, could efficiently emit visible light at room temperature, has stimulated a considerable amount of experimental and theorectical research. The technological interest in this material arises largely from the potentail applicability in the production of silicon based optoelectronic devices. In this article a brief overview of the properties of porous silicon is presented followed by a review of the formation mechanisms of porous silicon and the theoretical models proposed to explain photoluminiscence in PS. Lastly some other technological and scientific uses of porous silicon are mentioned.

I. INTRODUCTION

Nearly forty years ago during the electropolishing of silicon in aqueous hydroflouric acid, A.Ulhir[1] stumbled upon a strange form of silicon. Upon observation it was seen that this material had pores that grew into the crystalline structure from surface downwards [fig.1]. Each pore was seen to give -rise to secondary pores and so on, much like a fractal, giving rise to a vast labyrinth of permeating pores. As a result of this mesh or network of pores, this new form of silicon has a very large surface area and acts as a strong adsorbent. This material was therefore named porous silicon(PS).

Silicon has been regarded unsuitable for optical applications for quite a long time. The major drawback comes from its indirect bandgap which leads to very low quantum efficiencies of photoluminiscence (PL) and of electroluminescence (EL). It was thought that a semiconductor light source such as a light-emitting diode(LED) or a laser diode(LD) cannot be made from silicon. The inability of silicon to emit light seriously compromises our ability to realise optoelectronics circuits based on silicon. In 1990 Canham [2] started a new area of technological speculation with the discovery that highly porous silicon(PS) could efficiently emit visible light at room temperature. The quick and easy reproduction of the result in laboratories around the world has led to a highlight in porous silicon research during the recent years. Semiconductor physicists and material researchers have been excited by this breakthrough and it seems that the "holy grail" of realising all silicon based optoelectronics has become realistic.

In this paper the preparation techniques, the morphology and the properties of porous silicon will be reviewed. The proposed formation mechanisms of PS and the models for photoluminiscence will also be discussed. In conclusion some of the important technological uses of porous silicon (PS) will be mentioned.

II. PREPARATION AND FORMATION MECHANISMS OF POROUS SILICON

II.1 Preparation technique

PS is routinely produced by eletrochemically etching a silicon wafer in a hydrofluoric acid solution at relatively low current densities. In the electrochemical cell the silicon wafer, typically a [001] or [100] grown single crystal, constitutes an anode, while an inert metal like platinum is the cathode. The formation process of the porous layer at the silicon anode is very sensitive to (i) concentration of HF in the solution, (ii) the current density during the reaction, and (iii) the type and amount of dopant in the substrate. In text the typically used electrolyte is $1:1$ ratio of 10 to 50 percent HF and ethanol while typical current densities range from $2mA/cm^2$ to $200mA/cm^2$. Fig.1 shows the XTEM of a [100] arsenic doped silicon anodized in 10 percent HF at $10mA/cm^2$ [fig.1].

II. 2 Porous Silicon Formation Mechanisms

Although porous silicon has been extensively studied, the exact mechanisms for its formation are not well understood. Various models have been proposed. We shall mention three popular models.

II.2.1 The Beale model

The basic premise of this model is like the theories on electrostatic discharge and dielectric breakdown where the E field lines concentrate at surface irregularities, focus current flow at the PS pore tips and locally enhance dissolution there. In 1985 Beale *et al.*[3] noticed that the dc electrical resistivity of dry PS is close to that of intrinsic Si and concluded that the interpore regions were devoid of mobile carriers due to overlapping depletion regions. Current was therefore selectively directed to the pore depths as a result of the high resistance depleted porous structure. To obtain the necessary depletion in both n and p type silicon under anodisation potentials, it was necessary to assume Fermilevel pinning at midband gap. The primary advantage of the Beale model is its construction in terms of familiar energy band diagrams, Schottky barriers and depletion regions. However, it is somewhat questionable whether in the silicon/HF system the Fermilevel is actually pinned.

II.2.2 The Diffusion-limited model

This model [4] describes the formation of PS in terms of a stochastic random walk. During pore generation, a hole diffuses to the silicon surface and oxidatively reacts with a silicon surface atom. The nature of random walk presents the pore tip as the most likely contact site for a particle diffusing from the bulk of the semiconductor and provides a similar selective dissolution at surface irregularities as does the Beale model. A characteristic diffusion length which is a function of dopant concentration, current density, etc controls the different pore morphologies. Unlike the Beale model, the tenants of this model are not restricted to diodes but apply universally to all electrochemical phenomena.

II.2.3 The Electrostatic model

This model [5] assumes the formation of a passive layer (*eg.* an oxide layer) at the surface of the pores, such that the electrolyte is never in direct contact with the substrate. Accordingly, pore formation is a consequence of the dissolution of the passsive layer enhanced by the microscopic electric field. The competition between the growth and the dissolution of the passive layer gives rise to a time evolving electrolyte/passive layer interface which defines the surface of the pore. This model predicts the correct dependence of pore size on HF concentration.

Also, some groups have used fractals and neural networks to explain the structure of pores in porous silicon.

III. PHOTOLUMINISCENCE IN POROUS SILICON

III.1 Photoluminiscence characteristics

When a sample of porous silicon is irradiated with ultraviolet radiation, it is seen to glow an orange/red colour. This photoluminscence of PS shows characteristics that are commom to very differently prepared samples. The prominent amongst these characteristics are listed below.

1. PL spectrum is clearly observable (*ie.* distinguishable from background noise) in the region $6000 - 9000$ angstroms [fig.2].

2. The peak of the PL spectrum lies between 7500 and 8000 angstrom [fig.2].
3. The position of the peak of the spectrum may change a little with the preparation of the sample but the range does not vary too much.
4. The spectrum is nearly bell-shaped.
5. The photoluminiscence remains stable upon annealing upto 300 degrees celsius [fig.2].
6. The photoluminiscence shows a sharp decline between 350 and 550 degrees celsius[fig.2].
7. The spectrum shows a blue shift as the width of the silicon columns (wires) decreases.
8. The spectrum shows a blue shift when the sample is subjected to pressure.

III.2 Photoluminiscence mechanisms

The phenomenon of photoluminiscence in PS is even less undestood than porous silicon formation. A variety of possible mechanisms have been suggested. The quantum confinement model[1,6] was the first to be proposed. Others such as $a-Si:H$ model[7], the silicon hydride complexes model[8], the siloxene model[9] and surface states of crystallites[10] have been proposed. Of these the more supported ones are:

III.2.1 Quantum confinement model

Silicon is a $1.1eV$ indirect band-gap semiconductor and hence not expected to emit light in the visible region. Therefore to explain PL, quantum confinement of carriers in porous silicon "wires" was proposed. Porous silicon has columns of "quantum width" extending into the structure. This model proposes confinement of the carriers in these wires. Such confinement increases the band-gap energy to about $1.5eV$ which can provide an explanation for photoluminiscence[6]. In addition, the peak in the PL spectrum has been shown to shift towards the blue as the thickness of the silicon wires decreases and recent evidence for direct charge confinement has been provided for PS. This is a widely accepted model.

III.2.2 Siloxene model

Siloxene is a layered compound formed by corrugated [111] planes stacked on top of each other. The in-plane coordination of Si atoms is 3. The remaining valence electrons are alternatively saturated by H and OH groups. Siloxene and its derivatives have been known for a long time for their PL properties. Soon after the discovery of PL in porous silicon, Brandt *et al.* proposed an explanation of the phenomena in terms of siloxene derivatives of the form $Si_6O_{3+x}H_{6-y}$. These complexes would be located at the interface between pores and the silicon skeleton. The basis for this proposal was the astonishing similitude of the PL signal, the FTIR and Raman spectra of PS with those of siloxene. The presence of oxygen has since been shown to be unnecessary to obtain photoluminiscence in PS. .

III.2.3 Silicon Hydride Complexes model

This model proposes that hydrogen-rich clusters (*eg.* $Si-H, Si-H_2$) are formed at the surface of the PS skeleton. These clusters have dangling H bonds which act as centers for radiative recombination resulting in emission of observed luminiscence. In experiments performed by the author, hydrogen is seen to evolve from PS at temperatures corresponding to $Si - H$ and $Si - H_2$ bond energies[fig.3]. Photoluminiscence is also amazingly seen to decay around these temperatures. This is also a popular model.

IV. CONCLUSION

IV.1 Technological importance of porous silicon

The properties of photoluminiscence and electroluminiscence with their implications in the field of optoelectronics have made porous silicon one of the most technologically important materials. However, besides this there are many uses of porous silicon. Its reactive porous nature allows for the selective formation of unique electronic components and mechanical naostrutures. the low temperature oxidation of porous silicon and the electrochemical conversion of PS to oxide has already been utilised in electronic isolation technology [silicon-on-insulator(SOI) and fully isolated porous oxidised silicon (FIPOS) processes]. Silicon displacement reactions within the porous network have produced various uniquely formed films and microstruture including thick stress-free films of silicon nitride/oxynitride, conducting tungsten films, and silicon carbide semiconductors. In addition, silicide formation has been used to produce other types of buried conductive regions.

Because of its extreme reactivity due to the large surface are of its pores, PS has been demonstrated as a useful sacrificial layer in micromachinery, and the selective, dopant dependant formation of PS has been used in profiling the impurity distribution in p type Si substrates. A modified porous silicon structure has been utilized as a high-field electron emission source. Porous silicon's unique morphology has also been employed in fabrication of chemical sensing microstructures. The chemical modification PS by silinization has been studied for use as ion sensitive membranes (ISFETs).

IV.2 Concluding Remarks

It is clear from the above discussion that porous silicon is a material of great technological and scientific importance. However, before PS is successfully implemented into standard fabrication repertoire and scientific use, a better understanding of the formation and properties of this unique material is required. This review summarizes the formation mechanisms of porous silicon, its special property of photoluminiscence with the underlying mechanisms and some potential commercial utilizations.

FIGURES

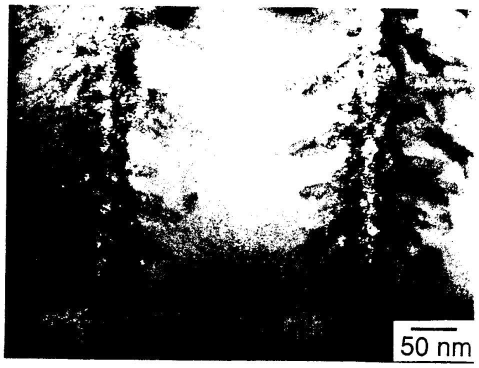

FIG. 1. *A porous silicon sample showing the distinctive pore morphologies. Two pore tips with numerous side branches. [12]*

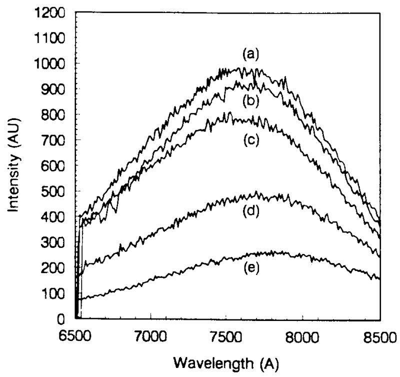

FIG. 2. *Photoluminiscence spectra of porous Si after a series of 5 min in situ thermal treatments at different temeratures: (a) as prepared, (b)* 300^oC*, (c)* 350^oC*, (d)* 400^oC*, (e)* 450^oC*. [11]*

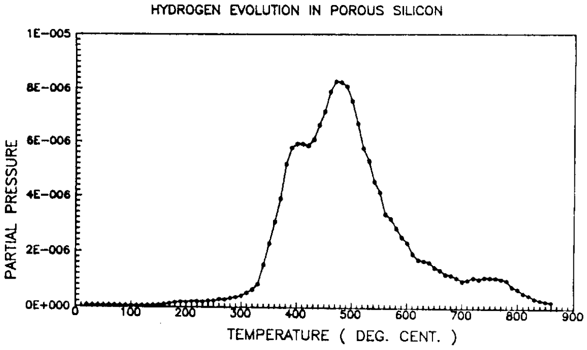

FIG. 3. *Evolution of hydrogen from porous silicon upon annealing from* 20^oC *to* 900^oC*. [13]*

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