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Reflectivity of Porous Silicon

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Abstract: Reflectivity of porous silicon (PS) has been studied on unannealed fresh PS films and on PS films annealed at 250 °C in vacuum. The reflectance spectra of fresh PS films do not change significantly after the annealing. There are two reflection edges, the first at about 1.1 eV (1100 nm) which corresponds to the band gap of crystalline silicon. The second edge occurs at approximately 1.6 eV (800 nm) which is due to absorption by the PS film. This gives an estimate of the band gap for our characterised films. It is consistent with the photoluminescence peak at 1.68 eV and suggests that similar origins, band edges, would be involved.

Key words: Porous Silicon, Reflectivity, Annealing, Band gap, Spectra

Introduction

Since the work of Canham, 1990, porous silicon (PS) has received enhanced attention due to its possible optical applications in light emission, associated with its well known micro-electronic applications. The "band gap" and optical reflectance are important parameters. Here We report studies of the spectral reflectivity of PS films, and the effects of annealing. The results complement and extend several previous studies of optical properties of PS films of varying types.(Lehmann and Gosele, 1996; Kolesar *et al.*, 1996; Bright *et al.*, 1997; L. Y. Chen *et al.*, 1994 and Pickering *et al.* 1994). Reflectance measurements have the advantage that normal thin films can be measured in situ, without the need to remove them from the substrate.

Experimental details: All the PS samples were prepared by a standard method Dariani *et al.* 1993, which has the advantage that the composition of such samples has been found to be $Si_{2.5}O_{1.2}C_{1.3}H_{1.2}$, along with a trace of fluorine. We used p-type Si wafers of thickness 0.28 mm, float-zone, (100) orientation and resistivity 10 Ωcm. An ohmic back contact was formed before anodisation by vacuum evaporation of Al, followed by vacuum annealing at 400 °C for 30 min. Awire was attached and the contact sealed with black wax. Anodisation was carried out in a teflon beaker with 50% HF at 10 mA/cm² for 5 min under ultrasonic agitation, at room temperature. The wafers were removed and dried without rinsing. The film produced had fine pores and was about 2 μm thick. Photoluminescence (PL) studies showed peak emision at about 740 nm and Electroluminescence (EL) studies showed a peak at 540 nm (Dariani *et al.*, 1994). The full width at half maximum of the EL band (about 86 nm) is nearly equal to that of the PL band (90 nm). These widths show that the films were relatively uniform.

A Cary-5 Spectrometer was used to measure reflectance spectra, using a band width of 0.5 nm. The spectra were obtained at room temperature in the wavelength range 400 to 1400 nm. Measurements were made on fresh PS, and PS that had been annealed at 250 °C for 30 min at 10^{-6} Torr and slowly cooled down to room temperature at the rate of about 1-2 °C/min. Such annealed PS samples have been found to show differences in scanning electron microscope (SEM) spectra (Dariani and Haneman, 1994), the annealed material showing well-resolved small egg-shaped particles which are barely discernible before annealing.

At the available precision, there were no significant differences observed between the reflectance spectra from fresh and annealed films. The data are displayed in Fig. 1. Note that there are two reflection edges. The first edge occurs at about 1.1 eV (1100 nm) which corresponds to the band gap of crystalline silicon. The second edge occurs at approximately 1.6 eV (800 nm) which is due to absorption by the PS film. This data is within the range of absorption data of Lehmann and Gosele (1996), Wang *et al.* (1993), Ito *et al.* (1992), and Koyama *et al.* (1991). Wang *et al.* (1993) prepared their PS film from a boron-doped Si wafer (15 Ωcm, (100)) at 10 mA/cm² for 20 min in a 1:2:7 (99 wt% ethanol : 48 wt% HF : H2O) electrolyte. Their data show that absorption begins at about 590 nm (2.1 eV) and then drops at higher wavelengths.

Ito *et al.* (1992) prepared PS films from boron-doped Si (111) wafer with low resistivity (<0.01 Ωcm) at 40 mA/cm² in a 1:1:2 (HF : H_2O : C_2H_5OH) solution. Our samples were prepared in a manner similar to their specimen (a). Their results show that absorptoin drops for wavelengths higher than about 800 nm, which is when the reflection would increase.

Koyama *et al.* (1991) prepared their PS layer from a p-type (111) 0.1 - 0.2 Ωcm Si wafer at 10 mA/cm² for 30 min in 20 wt% aqueous HF. Their data show that absorption drops for wavelengths higher than 700 nm, after which the reflection would increase.

Results and Discussion

Our data show that the onset of reduction of reflectivity, implying increase of absorption, occurs at about 800 nm (1.6 eV). The absorption edge from the above - described results Wang *et al.* (1993) and Koyama *et al.* (1991) is in the range of 590 - 800 nm, or 1.6 to 2.1 eV. Lehmann and Gosele (1996) reported values of the optical gap for free-standing films to be the order of 1.8 and 1.2 eV for high and low porosity materials respectively. It seems clear that the variation in the results for specimens from different sources is due to differences in the nature of the films. The porosity is undoubtedly one factor, but others could include the chemical composition which also varies with preparation conditions. Our results are within the spread, and consistent in particular with those of Ito *et al.* (1992), whose method of film preparation was closest to ours.

It is of interest to compare the optical band gap, which we regard as an average parameter for the film, with the energy of photoluminescence. (The EL is very weak (Dariani *et al.*, 1994) and not belived to be representative of the major part of the material.) As mentioned, the peak of the PL in our films occurred at 740 nm, or 1.68 eV, which is close to the onset, of reflectivity reduction observed at ~ 800 nm, i.e. the optical band gap. Derivation of the precise value of the band gap of a semiconductor from optical absorption is a non-trivial matter which requires an expression for the shape of the absorption or reflectance as a function of light energy. The nature of the band gap in PS is still subject to discussion. It could be the crystalline Si band gap, broadened by quantum confinement effects in small particles. However a reliable theoretical expression for the optical absorption is not available for PS, and in any case the film differs from a single crystal in that the properties are less homogeneous. Therefore we cannot give a precise value for the average band gap in our films, but only an estimate that it is near 1.6 eV.

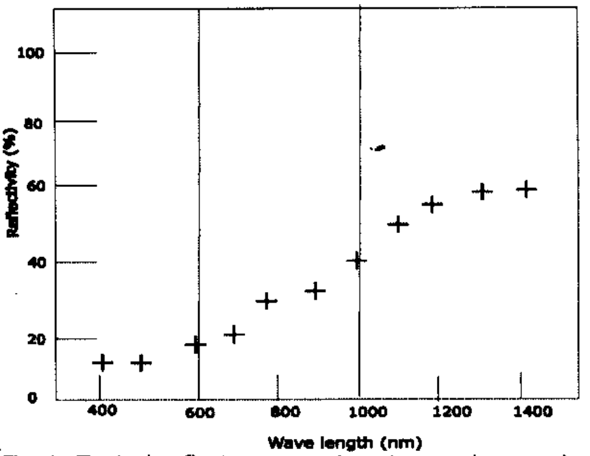

Fig. 1: Typical reflectance spectra at room temperature from freshly prepared PS, or from PS after annealing in vacuum for 30 min. at 250 ºC.

The difference between this and the PL peak at 1.68 eV may or may not be significant, but it is sufficiently small that one may conclude that the PL is due to carries recombining either across the average band gap, or between levels close to the average band edges.This suggests that the PL is a recombination phenomenon that has a similar average dependence on the properties of the whole film as in the case of the reflectivity. In other words, it is consistent with the origin of the PL being a general band effect rather than due to impurities.

The negligible effect of the annealing at 250 ºC is of interest since, as mentioned, the SEM topographs show changes Dariani and Haneman, (1994). The explanation provided for the latter has been that a thin film non-conducting coating on quantum-sized spheroidal particles gets reduced by the heat treatment. From the present studies, it appears that such changes have no discernible effect on the reflectance properties. This is reasonable if the coatings are very thin, as has been surmised.

Conclusions

In conclusion, the results from our samples show that there are two absorption edges. One corresponds to the band gap (1.1 ev) of crystalline Si on which the film is deposited. This is consistent with the low absorption of PS. The other edge comes from Ps itself (~ 1.6 eV). For light energies in the range 1.1 to 1.6 eV, the optical absorption is due to the crystalline Si substrate, and for energies greater than 1.6 eV, the absorption is due to both crystalline Si and PS. The reflectance edge and PL peak are at similar energies. Heat treatment up to 250 ºC does not appear to affect the reflectance significantly.

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