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An Investigation of Porous Silicon by Means of Positron Annihilation

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Abstract. Positron lifetime spectroscopy has been used to investigate a porous silicon film subjected to heat treatments up to 1170°C. Annealings between 300 and 500°C resulted in a 17% mass increase of the film due to oxygen uptake following the effusion of hydrogen. The positron data also indicate that vacancy clusters are formed in the silicon oxide layer or the silicon oxide—silicon interface surrounding the nanocrystallites as oxygen replaces the effusing hydrogen. The vacancy cluster concentration, which may have a bearing on the photoluminescent properties, increased by a factor of three with heating to 500°C and then decreased to one-third the original value at higher temperatures. Above 900°C vacancy migration and clustering occurred, accompanied by visible deterioration of the film.

Keywords: positron annihilation, porous silicon

Introduction

The mechanism responsible for light emission from porous silicon is not yet fully understood but it is apparent that the silicon surface, with its defects, plays a dominant role in determining the luminescent properties. The nature of the surface in porous silicon, in turn, depends on a host of factors related to the preparation of the material and its subsequent treatment. Because the surface area in porous silicon is extremely large, it lends itself to investigation by the use of positrons as demonstrated in an earlier work [1]. In this particular study, we have used the positron annihilation technique to investigate porous silicon which has been subjected to heat treatments in an argon atmosphere with the aim of identifying significant changes in the surface structure.

The positron technique is particularly well suited to this type of investigation for a number of reasons. In general, positrons injected into a material may undergo several modes of annihilation. Following rapid thermalization some will annihilate in the bulk material with a lifetime characteristic of the material while others may become trapped at neutral or negatively charged vacancies or vacancy clusters where they subsequently annihilate. The number of trapped positrons depends upon the vacancy concentration and, as a consequence of the reduced electron density in open volume defects, the positron lifetime becomes longer than the bulk value by an amount which depends in part on the open volume. Conditions permitting, some positrons may form positronium i.e. a bound state between a positron and an electron. The probability of this occurrence depends on several factors, a critical one being the availability of sufficient space to accommodate the positronium atom. Positronium is formed in two states, parapositronium (spin 0) or orthopositronium (spin 1) in the ratio 1 : 3. Parapositronium undergoes rapid self-annihilation with a lifetime of 125 ps while orthopositronium, which has a vacuum lifetime of 140 ns, normally undergoes so-called pick-off annihilation with another electron in the medium, thus reducing its lifetime from 140 ns by an amount strongly dependent on its environment.

Experimental

The porous silicon used in this work was produced by the anodization of p-type crystalline silicon in a solution of 50% hydrofluoric acid in ethanol (4 : 1) for 22 min at a current density of 57 mA/cm^2. The resulting

layer was 94 μm thick and had a porosity of 69% as determined gravimetrically. In order to have some control over oxidation that occurs at high temperature, heat treatments were performed under flowing high purity argon in a quartz tube. The samples were placed in the pre-heated tube for 1/2 h following which they were rapidly cooled to room temperature while remaining in the argon atmosphere. This procedure, of course, does not preclude oxidation since there will still be air present in the pores and adsorbed on the surfaces despite the argon ambient. After cooling, the samples were exposed to air for the 2–6 days required for the positron experiments following each heat treatment.

The positron lifetime measurements were performed at room temperature with a lifetime spectrometer having a time resolution of 200 ps. The positron source consisted of 15 μCi of ^{22}NaCl deposited very uniformly over an area of about 1 mm^2 on a 0.8 μm thick aluminum foil resulting in a very small source contribution of 2% intensity and a lifetime of 250 ps. The computer analysis of the lifetime spectra is described in Ref. [1].

Results and Discussion

Positrons emitted from ^{22}NaCl have a maximum kinetic energy of about 400 keV. With the porous layer thickness in the present case, about two-thirds of the positrons have sufficient energy to pass through the layer and become thermalized in the silicon backing where they annihilate with the $\sim$217 ps lifetime characteristic of bulk silicon. The less energetic positrons are thermalized in the silicon skeleton of the porous layer and, because the diffusion length of the positrons is much greater than the typical size of the nanocrystallites, the positrons will be rapidly deposited near or at the surface or in the pores. Since the sample has been exposed to the atmosphere, the surface region will consist of a native oxide layer likely containing vacancy-type defects where some positrons may be trapped. Positrons which are not trapped, and therefore pass through the surface layer can form positronium which either remains attached to the surface or escapes into the pores.

To obtain reasonable goodness-of-fit values for the lifetime spectra, five lifetimes, τ_1 to τ_5, with associated intensities, I_1 to I_5, were required. The ability to resolve this unusually large number of components results from the lifetime components being very well separated: typical lifetimes were 0.12, 0.2, 0.4, 3, and 50 ns. The extraordinarily long 50 ns lifetime is surely due to orthopositronium in the pores. Thus the τ_1 component, with a lifetime of about 125 ps, is due to the self-annihilation of parapositronium (and therefore provides no additional information about the medium in which it annihilates). The next longest lifetime, τ_2, had an average value of 217 ps which is the positron lifetime in crystalline silicon. The intensity of this component, which we label I_{217}, is a direct measure of the fraction of positrons penetrating the porous layer. This provides the opportunity to monitor the mass of the porous layer as the heat treatments proceed since I_{217} decreases as the mass (per unit area) increases according to

$$I_{217} = \mathrm{e}^{-\alpha \cdot t} \tag{1}$$

where α depends directly on the layer density (as well as the positron energy) and t is the thickness of the layer. Figure 1 shows the fraction of positrons passing through the porous layer to the backing as a function of annealing temperature. The increase in I_{217} between 20 and 200°C reflects a slight decrease in mass of the porous layer likely due to the desorption of adsorbed gases. Between 300 and 500°C there is a significant increase in mass which is attributed to the incorporation of oxygen to form silicon oxide replacing the hydrogen which is known to effuse in this temperature range [2]. This observation is in accordance with infrared spectroscopy measurements which show that the

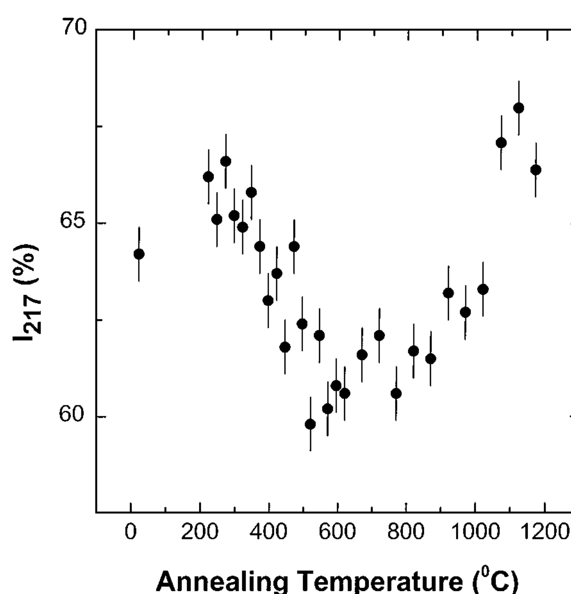

Figure 1. The percentage of positrons, I_{217}, transmitted through the porous layer as a function of annealing temperature.

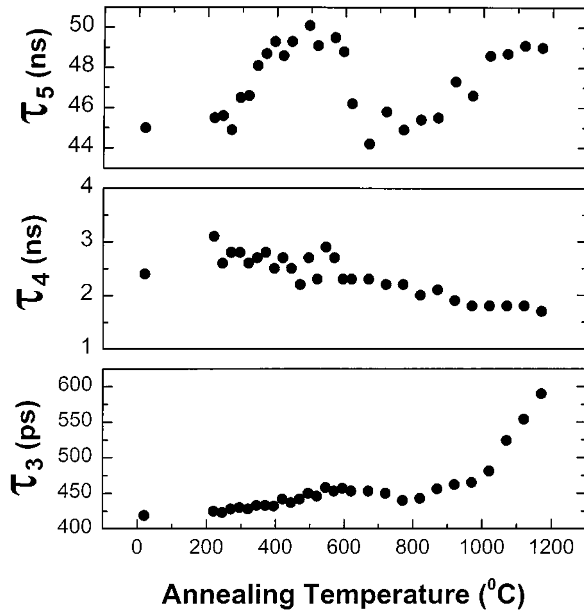

Figure 2. Porous layer positron lifetimes as a function of annealing temperature.

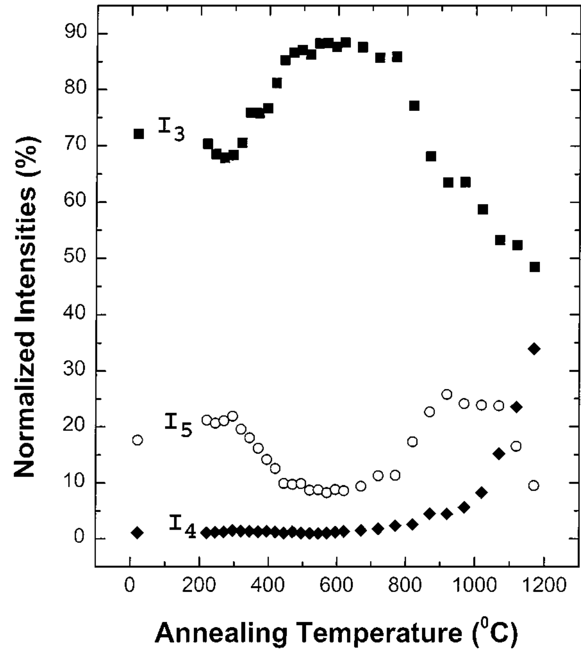

Figure 3. Intensities of the lifetime components for the porous layer normalized to the fraction of positrons annihilating in the layer.

disappearance of Si—H bonds is accompanied by the appearance of Si—O bonds [3–5]. The increase in mass is calculated to be 17% which means that the number of oxygen atoms incorporated is about one-third of the number of silicon atoms present. As suggested above, the source of the oxygen is likely the air adsorbed on the pore walls. After annealing at 1000°C the porous layer was visibly damaged and beginning to separate from the substrate which would account for the increase in the number of positrons reaching the substrate.

The remaining three lifetime components are believed to be associated with the porous layer itself. Their lifetimes and intensities (normalized to the percentage of positrons annihilating in the layer) are shown in Figs. 2 and 3. The lifetime τ_3 is attributed to positrons which are trapped in vacancy clusters in the silicon oxide layer or the silicon oxide–silicon interface since its value of about 450 ps is substantially larger than the 235 ps lifetime found in SiO_2. Using I_3, which depends on the vacancy concentration, the relative change in the vacancy cluster concentration, R, may be calculated. The result in Fig. 4 shows that the concentration increases by a factor of three during oxygen uptake to 500°C; at the same time, the near constancy of τ_3 shows that the vacancy clusters are not significantly different from those present initially. When the oxygen uptake has ceased above 600°C, the concentration decreases eventually reaching its original value at 800°C. The

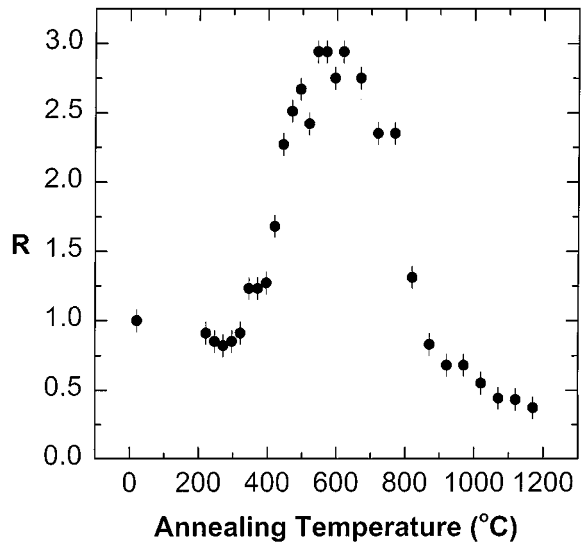

Figure 4. Vacancy cluster concentration relative to 20°C as a function of annealing temperature.

still nearly constant τ_3 suggests a thermally induced relaxation not involving vacancy migration. The further decrease in concentration at higher temperatures, coupled with the increase in τ_3, suggests the onset of vacancy migration with the formation of larger clusters. This vacancy behaviour may have a bearing on the reduced photoluminescence as porous silicon is oxidized

since vacancy clusters are potentially non-radiative recombination centres.

The τ_4 component is attributed to positronium trapped at surface defects. The dramatic increase in its intensity above 1000°C is likely accounted for by the severe structural change suggested by the visible deterioration of the layer. As noted above, the τ_5 component is due to positronium in the pores. Its very long lifetime indicates very weak interaction with the pore walls. However, there is a sharp decrease in τ_5 at about 600°C pointing to a stronger interaction which may result from the α-ß phase transition which occurs in SiO_2 near this temperature. In Fig. 3 it is noteworthy that as I_3 increases, I_5 decreases. This supports our earlier interpretation [1] that the vacancy traps in the oxide layer surrounding the pores determine the amount of positrons which enter into the pores to form positronium.

Conclusion

The positron annihilation technique has been used to quantify the uptake of oxygen as it replaces effusing hydrogen during heat treatment of porous silicon. In the present case the oxygen incorporation amounted to one-third of the silicon atoms present in the porous film after the sample was annealed at 500°C. The growth of the silicon oxide layer was accompanied by a three-fold increase in the concentration of the associated vacancy clusters. The concentration gradually decreased by means of relaxation above 600°C and vacancy migration creating voids occurred above 900°C. A dependence of photoluminescent properties on vacancy cluster concentration is inferred.

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