A study of porous silicon prepared under different HF concentrations by positron annihilation

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Abstract

Two-dimensional angular correlation of positron–electron annihilation radiation and positron-lifetime experiments have been performed on lightly doped porous silicons prepared under different HF concentrations. Positronium formation in the etched pores and positron trapped in voids are observed in both experiments. A surprising result is found that both positron lifetime and momentum spectra show a reduction in the size of the etched pores with decreasing HF concentration in the etching solution. This trend is different from the intuitive expectation that the pore size increases with increasing porosity. Our result can be explained in terms of the formation mechanism of porous film in lightly doped silicon. © 1998 Published by Elsevier Science B.V.

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1. Introduction

Porous silicon formed by electrochemical etching in HF solutions [1] has been widely investigated. The low-temperature oxidation [2–4] of porous silicon makes it suitable for use in silicon-on-insulator structures in integrated-circuit technology. Its strong photoluminescence [5–7] shows the possibility for applications in Si-based optoelectronic devices and displays. To understand the interesting phenomena and put into commercial utilization, it is important to know the effect of the anodization condition on the microstructure of porous silicon. The microstructure of heavily doped silicons, with resistivity from 0.065 to 0.01 Ωcm for p-type and 0.025 to 0.006 Ωcm for n-type, has been widely studied by high resolution

transmission electron microscopy (TEM) [8] and scanning tunneling microscopy [9]. It is found that porous silicon consists of many long pores with good shape and is perpendicular to the surface [10]. Their pore size distributions have been studied by using gas adsorption techniques [11,12]. However, unlike the heavily doped silicons, in the lightly doped silicons the pore structures consist of very small and randomly shaped pores and no clear individual pores can be found. To determine the detailed microstructure is very difficult. The pore radii are even beyond the measurable size of gas adsorption techniques. Nevertheless, the porous film produced from lightly doped silicon shows the strongest luminescence intensity among all the porous silicons reported today [5]. It is an excellent candidate for the use in Si-based

optoelectronic devices. Thus, an understanding of the porous formation in lightly doped silicon is desirable.

The above difficulty can be overcome by using the technique of positron annihilation measurements. Positron annihilation technique is a very sensitive tool to study voids and vacancies in a solid [13]. Because of their positive charge, positrons have a great probability to be trapped inside a void or vacancy, and the annihilation event will reveal the character of that void and vacancy. When the positrons are injected into a sample with a large free volume like the porous silicon studied here, they quickly thermalize in the order of 10^{-12} s and the large free volume will provide enough space to let the positron capture an electron and form a positronium. The spin-zero positronium, which is called para-positronium, has a lifetime about 125 ps and a very small momentum compared with that of the electron in bulk. With the measurement of the momentum distribution, the para-positronium shows a very sharp peak around zero point and can be resolved easily. The full width at half maximum (FWHM) of the momentum spectrum of the para-positronium will correspond to the size of the free volume [13]. The spin-one positronium, which is called ortho-positronium, has a lifetime about 142 ns. Such a long lifetime enables the positronium in a free volume to pick an electron from the surface and annihilate, and it is called the pick-off annihilation which has a lifetime about 10 ns. This lifetime is much longer than that of the positron annihilation in bulk. We can also obtain this pick-off component from the measurement of the positron-lifetime spectrum. The measured pick-off lifetime is determined by the size of the free volume and the boundary condition of the surface layer around the free volume [13].

Several works of positron studies on porous silicon have been reported recently. Cruz et al. first measured the positron-lifetime spectrum of porous silicon and decomposed the spectrum into three lifetime components by the “POSFIT” program [14]. They found that the intermediate component on the order of 500 ps strongly depends on the sample preparation conditions and annealing temperatures. Itoh et al. measured the lifetime spectrum and the Doppler broadening spectrum on a thicker porous

silicon sample [15]. They proved the existence of the positronium by the observation of an extra long-lived component (25 ns) and a sharper Doppler broadening distribution compared with that of silicon crystal. Suzuki et al. observed a dramatic change on the long-lived lifetime with the sample temperature and annealing temperature [16]. In our previous report [17], we made the first study of the electron–positron momentum distribution of porous silicon by two-dimensional angular correlation of electron–positron annihilation radiation (2D-ACAR). With the higher resolution of the technique than that of the Doppler broadening, we identified the location of the positronium state and estimated the average size of the etched pores. In this paper we present the positron-lifetime spectrum and electron–positron momentum distribution of a series of lightly doped porous silicon prepared under different HF concentrations. In addition to the observation of the formation of positronium, the surprising result is found that the average size of the pores where the positronium annihilates decreases with decreasing HF concentration, which is in contrast with the intuitive expectation. The reason for this peculiar behavior will be discussed in terms of the formation mechanism of the porous layer in lightly doped silicon.

2. Experimental

The silicon wafers used for our measurements were (100) oriented p-type single crystal with resistivity 10–20 Ω cm. Aluminum was evaporated onto the back as an electric contact. Samples were electroetched under a fixed current of 3.25 mA/cm² and three different etching solutions. The corresponding ratios of HF, H₂O, and C₂H₅OH for the etching solutions are 2:3:5, 4:6:5, and 6:9:20, respectively. The thickness of the porous silicon layer is about 200 nm.

The momentum spectrum of the porous silicon was measured by 2D-ACAR. The positron source was a 30 mCi ²²Na focused by a magnetic field of 1 tesla. The 2D-ACAR spectrometer has the following configuration. Two sets of two-dimensional gamma ray detectors were separated from the sample by 17.11 m and 18.6 m, respectively. Each gamma ray detector consists of 64 photomultipliers attached to a

single NaI(Tl) scintillator with a diameter of 50 cm and thickness of 1 cm. 2D-ACAR spectra were recorded as the angular distribution of the two gamma ray events. The angular resolution of our system is about 0.6 mrad. Typical 2D-ACAR spectra were collected by about 10^7 events.

The positron-lifetime spectra of the porous silicon were taken by measuring the difference between the time of the 1.27 MeV gamma ray emitted from ^{22}Na and the 0.511 MeV gamma ray from the annihilation of the electron and positron in the sample. The positron source ^{22}Na is sandwiched between two porous silicon samples. The events were taken from two sets of detectors which consist of a plastic scintillator and coupled to a fast photomultiplier and a fast electrical circuit. The resolution of our time spectrum is about 300 ps. Typical lifetime spectra were collected by about 5×10^6 events and decomposed into three components by the lifetime fitting program “POSFIT”.

3. Results and discussion

Figs. 1a,b show typical results of two-dimensional electron positron momentum distribution of pure silicon wafer and porous silicon sample, respectively. The spectrum of the studied porous sample is the sum of positron annihilation in the porous layer and the bulk silicon wafer. Comparing both spectra, the spectrum of the porous sample consists of one extra narrow and one extra broad peak at the center. The existence of the narrow peak clearly indicates the formation of positronium in the porous film. These two peaks are isotropic due to the random distribution of the pores. Because the central peaks do not show a clear difference between P_x and P_y direction, the spectrum has been circularly averaged to reduce the statistical error. The above observation suggests that the spectrum can be fitted by the contribution of the silicon wafer and two Gaussian peaks. The fitting equation is given by

$$N(P_r) = a_0 N_0(P_r) + a_n \exp\left(-\frac{P_r^2}{2\sigma_n^2}\right) + a_w \exp\left(-\frac{P_r^2}{2\sigma_w^2}\right), \quad (1)$$

where P_r is momentum, $N_0(P_r)$ is the spectrum of

Fig. 1. Two-dimensional electron–positron momentum distributions of (a) silicon wafer and (b) porous silicon etched under a fixed current of 3.25 mA/cm^2 and an etching solution with a ratio of HF, H_2O , and $\text{C}_2\text{H}_5\text{OH}$ of 4:6:5.

the silicon wafer, a_0 corresponds to the intensity of the silicon wafer, a_n , σ_n , a_w and σ_w correspond to the amplitude and the width of the narrow and the broad Gaussian peaks, respectively.

The intensity and the FWHM of the two Gaussian peaks of the porous sample prepared under different HF concentrations are shown in Figs. 2 and 3, respectively. First, let us consider the information obtained from the positronium formation in the narrow peak. In our previous report [17], we have shown that the location of the positronium is in the free volume of the etched pores rather than on the surface of the pores. From the uncertainty principle, the FWHM of the positronium momentum distribution ΔP will have an inverted relation to the space size ΔX occupied by the positronium. The result of our 2D-ACAR measurements shows that the pore size decreases with decreasing HF concentration. In

order to confirm this behavior, we have also performed the same experiment on the porous films prepared under a fixed current of 20 mA and different HF concentrations. It is found that the trend remains the same. This result is rather surprising because the less concentrated HF solution has been shown to produce the larger porosity as reported previously [10–12]. Intuitively one expects that the film with the larger porosity will have the larger pore size. However, this prediction is not true if we carefully examine the formation mechanism of porous films. According to the experimental and theoretical studies of the formation of lightly doped porous film [10], the porous film is fully depleted and its Fermi level is pinned near mid-gap as a consequence of a large density of surface states, and a Schottky barrier forms at the silicon–electrolyte interface. Because the depleted porous film has a high resistivity, the current flows down the electrolyte in the pores and into the substrate at the pore tips. The small pore tip radius can produce substantial field intensification leading to barrier lowering and hence an increase in current density. Since silicon is known normally not

Fig. 2. The dependence of the intensity and the FWHM of the narrow peak on HF concentration in the electron–positron momentum spectrum of porous silicon.

Fig. 3. The dependence of the intensity and the FWHM of the broad peak on HF concentration in the electron–positron momentum spectrum of porous silicon.

to be chemically attacked by hydrofluoric acid and the reaction takes place only if the silicon is anodic and a current is flowing, thus, in lightly doped silicon the dissolution is confined to the pore tips. It follows from the importance of the field enhancement effects, that the smaller the pore, the greater will be the barrier lowering on the pore and hence the greater the current flow and the growth rate. When a pore grows the enhancement effect is lost by increasing radii and a new protrusion will be formed. So the whole growth of porous structure in the lightly doped porous silicon is mainly contributed by creating new protrusions. In the less concentrated HF solution at a fixed current density, the larger porosity is caused by the larger growth rate due to the larger voltage drop across the interface. According to this explanation, a larger growth rate should correspond to a larger number of new etched pores which have a smaller size. Thus, decreasing the HF concentration in the etching solution will increase the number of pores and decrease the average size. This expectation is confirmed by our measurement of the intensity and the FWHM of the narrow peak in 2D-ACAR

spectra. As shown in Fig. 2, the intensity and the FWHM of the narrow peak increase with decreasing HF concentration which is consistent with our explanation.

The trend of the FWHM and the intensity of the broad peak is also similar to that of the narrow peak, i.e. they decrease with increasing HF concentration as shown in Fig. 3. The origin of the broad peak can possibly be attributed to the effect of the silicon nanocrystal, surface chemical compound, or vacancy cluster. The definite identification is still unclear and requires further investigation.

Our lifetime spectra of porous silicon were decomposed into three components and fitted by the "POSFIT" program. Figs. 4 and 5 show the dependence of the lifetime and the intensity of the middle and the longer components on the HF concentration in the etching solution, respectively. Although the intensity of the longer lifetime is about 0.5% only, the difference is still larger than the fitting error. The longer lifetime is in the order of 2–10 ns as shown in Fig. 4, it corresponds to the pick-off annihilation of positroniums. The magnitude of the pick-off positron lifetime is mainly determined by the size of the free

Fig. 4. The dependence of the intensity and the magnitude of the longer component on HF concentration in the lifetime spectrum.

Fig. 5. The dependence of the intensity and the magnitude of the middle component on HF concentration in the lifetime spectrum.

volume for which the positronium is trapped. A larger free volume results in a longer lifetime. From Fig. 4 we obtain that with increasing HF concentration the lifetime increases and the intensity decreases. This implies that the size of the etched pores increases and their number decreases with increasing HF concentration. This trend is in good agreement with that obtained from the narrow peak in the 2D-ACAR spectrum.

From Fig. 5 we can see that the middle lifetime is in the order of 0.5 ns, and its magnitude increases with increasing HF concentration. This value is approximately equal to the lifetime of the positron trapped inside a vacancy cluster. A smaller vacancy cluster will lead to a smaller lifetime of the trapped positron. If the middle lifetime is contributed by the positron trapped in a vacancy cluster, we will have the result that a smaller HF concentration will produce a smaller vacancy cluster. The trend of the middle lifetime is the same as the result of the broad peak in momentum spectra. Probably, they may correspond to the same positron trapping mechanism.

4. Conclusion

In conclusion, we have performed 2D-ACAR and positron-lifetime measurements on lightly doped porous silicons prepared under different HF concentrations. The formation of positronium can be clearly identified from the observation of the narrow peak in the momentum spectra and the long-lived component in the lifetime measurements. From the result of positron lifetime and 2D-ACAR we found that the number of pores increases and the average pore size decreases with decreasing HF concentration in the etching solution. It contradicts with the intuitive prediction that the pore size increases with increasing porosity. This peculiar behavior can be explained in terms of the formation mechanism of the porous layer in lightly doped silicon.

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