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A COMPARATIVE STUDY OF TRANSITION STATES OF POROUS SILICON BY SURFACE PHOTOVOLTAGE SPECTROSCOPY AND TIME-RESOLVED PHOTOLUMINESCENCE SPECTROSCOPY

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Abstract—It is shown that a series of electronic transition states in porous silicon were observed directly by surface photovoltage spectroscopy. As compared with the results of time-resolved photoluminescence spectroscopy on the same samples, the identification and correlation of transition states and luminescent bands in the porous silicon are presented. The results show that the transition and luminescent bands in porous silicon depend on the anodizing conditions. The observation is in good agreement with the previous theoretical calculations of the electronic structure and luminescent transition. According to the experimental and theoretical results, the transition bands are attributed to quantized Si wires with the different sizes. This result is distinctly helpful for the understanding of the luminescent mechanisms in porous silicon. Copyright © 1996 Elsevier Science Ltd

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1. INTRODUCTION

Recently, a porous silicon field is most active since Canham's discovery [1] that PS layers could efficiently emit visible light at room temperature. The past years have provided a colorful background of ideas that have come and gone, which involve either quantum confinement [1–2], luminescence from the hydrogenrich passivation layer [3], or luminescence from a siloxene derivative [4]. Although these models are currently under debate, some experimental evidence [1, 5] and theoretical works [6] strongly support the quantum confinement which originates from the creation of quantum size Si wires, leading to light emission in the visible spectrum.

Because of various perceived shortcomings of experimental evidence and the difficulty in characterizing the optical and electronic properties of porous silicon, the optical and transition properties of porous silicon are not thoroughly understood yet, and some explanations still remain controversial. More experimental results are required to clarify the mechanism of luminescence mainly due to the structural complexity of porous silicon. In this paper, the surface photovoltage spectroscopy (SPS) and time-resolved and steady-state luminescence spectroscopy were used for the investigation of porous silicons. The SPS indicates that there is a larger band gap in porous silicon than in bulk crystalline silicon and a group of peaks present in the range of 2.40-3.40 eV, which become dependent on the feature size of the silicon wires. Several luminescence features of porous silicon, emerged from the energetic position of 1.40-2.40 eV at different delay times, are resolved by time-resolved luminescence spectroscopy. Based on these experimental evidences and the previous theoretical calculations of the electronic structure, we identify these photovoltaic and luminescent bands and propose a possible model for the relationship between the transition and the photoluminescence. Our results show that the bands of the photovoltage and luminescence in porous silicon are concerned with Si wires with different feature sizes and surface states. This experimental finding provides a clear signature of the electronic structure and transition and indirectly confirms the existence of quantum size Si wire in porous silicon.

2. EXPERIMENTAL

2.1. Preparations of porous silicon

The investigated porous silicon samples were formed electrochemically from p-type, Boron-doped silicon wafers with (111) orientations and 5-8 ohm-cm resistivities. Wafers were cleaned prior to anodization according to a conventional method. Anodization was done with a two half-cell configuration. A liquid electrical contact was made to the wafer back side using a chamber filled with saturated KCl. The front side of wafer was exposed to ethanol solution of hydrofluoric acid. Porous silicon etching reactions were carried out at anodic current density of 0.2- 0.8 mA/cm^2 for 90 min in a HF concentration of 25% (w/w). The thickness and porosity of porous silicon was adjusted by varying the current density of etching under the conditions described above. The scanning electronic microscopy (SEM) was performed to observe the morphology of the porous silicon, which shows that the porous silicon are in a mesh structure with many even pores.

2.2. Measurements of SPS

In our experiment, measurements of SPS were carried out with a solid junction photovoltaic cell ITO/PS/c-Si/ITO using light source-monochromator-lock-in detection technique. The principle and setup diagram of SPS measurement were described in detail elsewhere [7, 8]. Monochromatic light was obtained by passing light from the 500 W xenon lamp through a double-prism monochromator (Hilger and Watts, D300). A lock-in amplifier (Brookdeal, 9503-SC) synchronized with a light chopper was employed to amplify the photovoltage. The spectra were normalized to unity at their maxima and the feature peaks of xenon lamp were deducted by a computer.

2.3. Measurements of photoluminescence spectra

Time-resolved measurements were performed with an acousto-optic modulator, photomultiplier and a gated photon counter. THG of electro-optical Q switch TAG is used as excitation source for luminescence (wavelength = 355 nm, pulse during = 10 ns). The peak intensity of laser light on the sample is about 30 kw/cm^2 . The signal from porous silicon is collected by a relative aperture 1:3 lens into a monochromator and detected by the photomultiplier (R446, response spectra 187–870 nm). The data are saved and processed by a computer after collected by a boxcar. The responsivity of the optical system is corrected by standard light source with temperature 2865 K. In the steady-state PL spectra, the signals were recorded by a spectrofluorophotometer (shimadzu) under conditions of continuous excitation by a light source.

3. RESULTS AND DISCUSSION

The surface photovoltage effect, which consists of a change of the surface potential barrier due to illumination, has been successfully applied to the investigation of electronic processes in semiconductors. Measurements of surface photovoltage vs wavelength of light (i.e. SPS) have yielded information on surface parameters, band gap and distribution of surface states in semiconductors. Because the photovoltage arises from the creation of electron-hole pairs by photoexcitation, which provides information on absorption property, the SPS is allowed to detect an excitation process. It is a powerful tool to analyze the electronic structure besides absorption spectroscopy and photoluminescence excitation spectroscopy. Several groups, fabricated some metal/porous silicon/silicon structures by the different conditions, had measured the photovoltaic effect [9] and photocurrent response [10]. Yan et al. [11] reported an interesting result on photovoltage spectra of porous silicon and a high photovoltage was observed in the range of 1.10-2.50 eV. The photovoltaic response was thought to originate from the Schottky junction M/PS and heterojunction PS/Si. Because of the differences of the investigated samples and used methods, the variable results were obtained and each sticks to his own view. A porous silicon, which consists of silicon wires (porous layer) terminated by the oxygen- and hydrogen-rich layer (surface layer), is a complicated system, and the composition, structure and properties strongly depend on the etching condition. Just due



Fig. 1. (a) The configuration of the photovoltaic cell, (b) The energy band diagram for porous silicon in contact with ITO [13].



Fig. 2. SPS of porous silicons formed by varying the current density of etching: (a) p-Si (non-etched); (b) 0.2 mA/cm²; (c) 0.6 mA/cm²; (d) 0.8 mA/cm².

to the complexity, the various phenomena have been exhibited and some mechanisms have been proposed for the explanation of the interesting samples. In general, porous silicons prepared by the rigorous conditions such as the samples anodized by higher current density in the mentioned reports demonstrate the thicker surface layer which dominates the structural and optical properties. Wafers of Si subjected to the mild anodizations (lower current density) are characterized by the mesoporous silicon mostly without the surface layer [12]. The crystalline Si nanostructure, controlled the optical features, had been observed by TEM in these samples [12]. In our experiment, we just adopted this condition for the fabrication of the interesting porous silicons. The configuration of the photovoltaic cell is shown in Fig. 1(a), which actually includes the ITO/PS,PS/c-Si and c-Si/ITO interface. If the sample is illuminated by more intense incident light, the incident light can penetrate the ITO/PS and PS/c-Si interface. The response of the photovoltage results from the sum of two junctions concerning the porous silicon due to the same polarity [9]. In our measurement, the sample was illuminated by incident light with the mild intensity. The incident depth of the light is less than the thickness of the PS layer (about $2-5\,\mu m$). The light only reaches ITO/PS interface and far from the PS/c-Si interface, at least, in the UV region. The photovoltaic response from the sample could be dominated by the ITO/PS interface condition which is related with the quantum confinement energy of PS, because the potential drop/built-in field is changed by this interface. Based on the above considerations and Maruska's model [13], Fig.1(b) presents the energy band diagram for porous silicon in contact with ITO. With this consideration, a photo-excited process between transition states in PS can be reflected by the photovoltage.

Figure 2. shows the SPS of the porous silicons and non-etched silicon. First of all, it would be observed that the SPS of the porous silicon is strongly different from that of non-etched silicon and a group of peaks, emerged in the range of 2.4-3.4 eV, are shifted to shorter wavelengths in comparison with that of bulk Si. This shift experimentally illustrates a larger band gap in porous silicon than in bulk crystalline Si. Secondly, the SPS of porous silicon depend on the anodizing condition. It is noted that the main peak of the SPS is discretely shifted to shorter wavelengths with increasing current density of etching, and the intensity of the SPS in the range of 2.4-3.4 eV gradually also increases. In addition, the wavelength of the main peak at the lower current density reaches that of a side peak at the high current density. The most striking feature is that the response of SPS in the porous silicon in the range of 300-500 nm consists of several discrete peaks. Because SPS gives information on absorption and excitation features, all these SPS evidences directly confirm the existence of a series of electronic transitions states and the feature size dependence of the energy levels in porous silicon.

A systematic investigation has been presented of the effect of the anodizing condition on the formation of porous silicon. In the determination of HF concentration and anodizing time, the porosity of porous silicon increases with enhancing the current density [14]. Canham [1] suggests that as porosity increases, feature sizes begin to decrease. Here, feature size is the actual parameter of interest and porosity is simply used as an indirect indicator of relative feature sizes. Dramatic quantum size effect should occur as the feature sizes shrink below the Bohr radius ($\sim 5 \text{ nm}$) of the free exciton in bulk Si [15]. The quantum confinement effect increases the energy bandgap, resulting in a blue shift of the absorption edge (i.e. the onset of SPS) as shown in Fig. 2. Silicon wires of the different sizes are formed from crystalline Si during etching, and feature sizes decrease with the increase of the current density. As a result, the peak of the SPS is discretely shifted to the different wavelength with increasing the current density. Based on the above considerations, it would be expected that the Si wires with smaller feature sizes result in the appearance of transition states in the range of high energy.

The distribution of diameter and shape of Si wires in porous silicon is random. There are assorted Si wires in porous silicon, whose distribution is dominated by the anodizing conditions. According to quantum confinement effect [1] and some calculation models [11, 17], the distribution of diameter of quantized Si wires in porous silicon is discontinuous and size difference is monolayer of Si atoms. In other words, the effective diameter of the Si wires whose cross section has the



Fig. 3. Analysis of SPS according to the calculation in Ref. [16]: the curve of SPS (solid line) and the analyzed curves of SPS (dotted and dashed lines).

shape of a square with rounded corners is discrete and equal to the integral times of monolayer of Si atoms. The size distribution of the quantized Si wires leads to the discrete distribution of transition energy. The smaller the feature size of the Si wires, the shorter wavelength the transition bands are shifted to. When the feature size is close to the Bohr radius (~ 5 nm) of the free exciton in bulk Si, the quantum confinement effect becomes feeble, and the transition bands are the same as ones of the bulk Si. Buda [16] and Ohno [17] performed first-principles electronic structure calculations of silicon wire with diameters up to ~ 1.5 nm in porous silicon. In their calculation, the Si wires with 3×3 , 4×4 and 5×5 structure are considered, which have the characteristic diameter of 0.76, 1.14 and 1.56 nm. Surface Si atoms are terminated by hydrogen atoms. The results show that the bandgap in porous silicon is direct at the zone center and increase as wire diameter decreases due to quantum confinement. The calculation proves the existence of the several absorption bands of Si wires with the smaller feature size in the range of high energy, which is absent in absorption of bulk c-Si. In our experiment, several bands appear in the region of 2.0-4.0 eV. In comparison, our results of SPS are in excellent agreement with Buda's calculation for the three Si wires. According to these calculations, we try to analyze the SPS of porous silicon (sample c). The analyzed SPS is shown in Fig. 3. We find that the several overlapping peaks in the shorter wavelength of the SPS result from the quantized Si wires with the smaller three feature sizes, and the subbands are fitted with a feature size. It is



Fig. 4. Time-resolved photoluminescence spectra of porous silicon recorded after different delays relative to the end of a laser pulse: (a) Td = 10 ns; (b) Td = 100 ns; (c) Td = 500 ns; (d) the steady-state PL spectra (1: $\lambda_{ex} = 355 \text{ nm}$, 2: $\lambda_{ex} = 488 \text{ nm}$).

evident to illustrate that the discrete SPS bands in the range of the shorter wavelength originate from silicon wires with the three feature sizes (0.76, 1.14 and 1.56 nm wire). From these results, we expect that the investigated porous silicon contains quantized Si wires with various feature sizes including the 0.76, 1.14, 1.56 nm, which lead to the SPS bands in the range of high energy.

Figure 4 shows time-resolved photoluminescence spectra of porous silicon (sample c) measured at different delay time (Td) after exciting by the laser. The wavelength of main luminescence peak is dependent on delay time (Td) and shifts to a long wavelength with increasing the delay time. At the time of 10 ns, the spectra line shape is unsymmetric and the maximum of the luminescence appears at 465 nm with several side bands. When the recording time is delayed, the main peak in 465 nm gradually disappears and the side bands become evident. A further increase (500 ns) in the delay time results in the disappearance of some bands from the spectra, and the appearance of a symmetric and dominant band in 589 nm. This feature imply that PL spectrum of porous silicon consists of several bands, and these bands differ strongly by their luminescence lifetimes. The short-wavelength one is a fast process and the long-wavelength one is slow, which is consistent with the calculated radiative recombination rate [18]. We carefully look into the PL spectrum in the delay time of 10 ns (Fig. 4(a)). It is found that the PL spectrum is composed of several overlapping bands with different wavelengths. Observing the spectrum, we present these peak wavelengths of these bands. The first one is the sharp band in 465 nm and is characterized by a short luminescence lifetime and a high intensity. The second band appears in 510 nm. The third band corresponds to an emission with a long luminescence lifetime in 589 nm, which is seen by us and other authors in a steady-state luminescence spectra, and is the subject of most of experiments. In addition to the bands mentioned above, the other bands are located in 540 and 620 nm, respectively. The slowest PL band (589 nm) is the almost contrast background, while the other bands are additional signals.

Recent papers [1, 19] have provided evidences that porous silicon can emit light in two distinct bands: the originally discovered 'red' band in 580-800 nm and the newly identified high energy 'blue' band in 430-550 nm ('F' band emission). Red and blue band are both affected by oxidation or aging of porous silicon, however in a different way. The blue band becomes evident after oxidation or aging while the red luminescence exists in as-prepared porous silicon. Some PL decay experiments [20, 21] have proved that the bands are also distinguished by slow and fast luminescence decay fall in 10 ns and 10 μ s range for blue and red bands, respectively. The origin of the red bands have held identical views with the previous literature [1, 3, 4]while the blue bands are believed to come from SiOx film in Si wires [19]. Our results are in good agreement with the illustrations mentioned above. In our PL experiment, two groups of bands are resolved by different decay time. One group of bands, known as red band, are commonly observed in 580-800 nm and the others in 450-550 nm, featured by discrete and sharp peaks with a short PL decay time and strong intensity, are attributed to the blue band. These features suggest that there are two kinds of different PL mechanisms in porous silicon. To clarify the PL origins and find the relationship between the transition states and luminescent states in porous silicon, we make a comparison between the SPS and the timeresolved PL. It is found to the peak wavelengths of these luminescence bands in high energy are accurately fitted by the wavelengths of the lower energies of three Si wires (0.76, 1.14 and 1.56 nm wire). This result reveals that the several PL bands are related to these energy levels shown in the SPS. Nevertheless, we should note that the blue bands exhibit a strong emission. The phenomenon can not be explained only from the three Si wires. The emission from the other Si wires and surface layer (SiOx) would contribute to the blue bands.

The PL bands are in fact affected by a variety of complex phenomena such as relaxation processes, impurity scattering, and excitonic interaction. The PL spectrum of porous silicon is the sum of the various bands involving the band-to-band radiative recombination and the interface state recombination in different energy levels due to Si wires with various feature sizes and surface states. It is difficult to give a clear signature of excitation and emission in porous silicon. In our experiment, some excitation states and emission bands in porous silicon have been identified



Fig. 5. Proposed diagram of PL emission process in porous silicon.

and resolved by SPS and time-resolved PL (Figs 2 and 4). To provide a relationship between the excitation and the emission, we try to assign the transition bands in SPS and PL bands in time-resolved photoluminescence spectrum and propose a possible model to explain the photoluminescence in porous silicon. The proposed diagram of PL emission process in porous silicon is illustrated in Fig. 5. The Si wires with different feature sizes are formed from crystalline Si during etching. The feature size and the distribution depend on the anodizing conditions. Due to quantum confinement effect, the energy of electron and hole pairs increases in the quantized Si wires with nanometer sizes and the energy bands are shifted to a shorter wavelength with lowering the feature sizes of Si wires. In porous silicon, a series of energy levels are formed by each Si wire, for example, shown with obvious three bands 375, 510, 620 nm in the 1.14 Si wire (see Fig. 3). The transition states in porous silicon are consistent of these energy levels and surface states formed by hydrogen-rich layer and SiOx outside the Si wires. The PL bands are emitted via these energy levels. When the electrons are excited to the higher energy levels (photocreated states), localized electron and hole pairs are created inside quantized size wires. Because of the low possibility of recombination of electron and hole inside the Si wires, the localized carriers are transferred to the lower energy levels (including all lower matchable levels) or tunnel into the surface states outside the Si wire by a nonradiative relaxation process, in which they are trapped and wait for a suitable partner for luminescence. The lower energy levels and surface states serve as luminescent states. The electrons and holes recombine to yield light through the luminescence states. While the electrons are excited to the lower energy levels, photoluminescence is given out by way of either direct or indirect recombination (via the nonradiative relaxation process). Because the Si wires are separated and have considerable energy mismatch among them, it is expected that there are nonradiative relaxation processes between the levels formed only by one Si wire (itself) or between these levels and surface states outside the Si wire. On account of the origins and size distributions, position and rate (time) of the luminescence bands are different. These differences are manifested by the appearance of several PL bands with different luminescence lifetimes. Due to the different PL centres and transportation from upper to lower states [22], the time dependence of PL bands is exhibited. The PL band with a short decay time is emitted via the higher levels and SiOx layer (PL centre). The red PL with a long decay time is due to the lower levels and hydrogen-rich layer (PL centre). The surface states, served as one of luminescence centres, play an important role in luminescence of porous silicon. The position and intensity of PL bands are affected by them. The surface state, consisted of SiOx and hydrogen-rich layer in same porous silicon, is a leading luminescence centre. A SiOx layer is formed in the preparation or post-treatment of porous silicon, which corresponds to increasing the luminescence centres. The enhancement results in a strong PL band.

The steady-state photoluminescence spectra of porous silicon under condition of continuous photoexcitation with different excitation wavelengths (λ_{ex}) are shown in Fig. 4(d). A wide, structure-free band with a maximum at 589 nm is observed in 355 nm excitation, which is characterized by a symmetry and broad width at half maximum of the order of 0.1 eV. With increasing the excitation wavelength (488 nm), the PL peak is shifted to the lower energy and the intensity gets lower, i.e. disappearance of PL band in the side of short wavelength. It suggests that the partial bands generate optical transitions during the long wavelength excitation and high photon energy is required to excite electrons for PL band in the range of short wavelength. The results can be understood in terms of the above discussions. Based on these observations and considerations, it is expected that the PL spectrum could be contributed by several PL bands which result from the Si wires and surface states. The PL spectrum in Fig. 4(d-1) can be divided into several bands. The main band dominated the PL spectrum is located in 589 nm, the two subbands in the two sides of the main band are 620 nm and 565 nm, respectively, which widen the PL band.

In conclusion, porous silicon is in fact a diverse family of nanostructure materials with a surface layer. Energy levels depend on the Si wires with the different feature sizes and surface states. Because PL originates from these Si wires and surface layer, the bands appear in different wavelengths and luminescence lifetimes. These facts have been exposed by surface photovoltage spectra and time-resolved PL spectra in our experiment.

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