

Band Dispersions in Photoluminescent Porous Si

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(Received 1 December 1997)

The same band dispersions as those obtained from crystalline Si along the Γ - Δ - X symmetry line are first observed from photoluminescent porous Si independent of its microstructure and porosity using an angle-resolved photoemission technique. The electronic structures of porous Si observed in the normal photoemission, valence photoemission, and L -edge x-ray absorption spectra are interpreted consistently to result from the overlap of that of bulk crystalline Si and that relating to the receding valence structure, which is suggested experimentally to be linked to the luminescence origin. [S0031-9007(98)05828-1]

PACS numbers: 71.24.+q, 61.46.+w, 78.55.Mb

The origin of visible photoluminescence (PL) from porous Si (PS) has been discussed in terms of "bulk effects," "surface effects," or "as a combination of both effects." Among the major bulk effect models, the quantum confinement model [1], noncrystalline model [2], and the irregular structure model, in which some of the Si atoms are randomly removed [3], are included. In these models, the visible PL is related to the widening of the band gap which originates from the bulk structures. A surface layer or a surface defect [4,5] is another candidate responsible for the PL mechanism. Surface localized states, the energies of which vary depending on the widening gap, have also been discussed [6]. Photoelectron spectroscopy (PES) is a useful tool which provides information about bulk and surface density of states (DOS) which are clues for understanding the bulk and surface effects. Our earlier PES studies indicate that the surface band gap of PS traces relatively well the PL peak energy which varies with the PS preparation conditions [7,8], suggesting that, at least to some extent, the surface electronic states are related to the PL origin. In this study, we have investigated the electronic structure in detail using a combination of angle-resolved photoelectron spectroscopy (ARPES), angle-integrated photoelectron spectroscopy (AIPES), and Si L -edge x-ray absorption spectroscopy (XAS) techniques. In this paper, we present the first observation of band dispersions along the Γ - Δ - X symmetry line from photoluminescent PS formed at the surface layer of a Si(001) substrate. The electronic states of PS observed in the spectra obtained using these techniques are consistently interpreted as arising from bulk crystalline Si DOS and structures associated with the receding valence states, which are suggested experimentally to be linked with the luminescent structure.

In order to understand the electronic structures of PS, we used two kinds of PS samples with different microstructures. These samples were prepared by anodizing p -type degenerate (0.01–0.02 Ω cm) and nondegenerate (4.5–6.0 Ω cm) Si(001) substrates in a mixture of 55 wt % aqueous HF solution and ethanol at a ratio of 1 : 2

at an anodization current density of 100 mA/cm² for 20–30 s. The present anodization conditions lie within the range of widely used anodization conditions for obtaining photoluminescent PS. It is known that the structure of PS formed with a ~ 0.01 Ω cm degenerate substrate becomes pillarlike with a dendrite structure, and that PS formed with a ≥ 1 Ω cm substrate has three-dimensionally a more isotropic porous structure than PS formed with a ~ 0.01 Ω cm substrate [9]. The measured porosities were $(55 \pm 5)\%$ and $(70 \pm 5)\%$ for the samples formed with a 0.01–0.02 and a 4.5–6.0 Ω cm substrate, respectively. The luminescence properties were confirmed by PL measurements using a 325 nm He-Cd laser. PL can be observed easily with the naked eye from both the PS samples formed with these different resistivity substrates where the PL intensity for PS on a 4.5–6.0 Ω cm substrate was higher than that for PS on a 0.01–0.02 Ω cm substrate by more than a factor of 100. The PL peak energies for these PS samples were almost the same and were in the range of 1.7–1.75 eV.

ARPES measurements were performed using the synchrotron orbital radiation (SOR) ring at the Photon Factory of the National Laboratory for High Energy Physics. Normal emission spectra in the [001] direction along the Γ - Δ - X symmetry line for the photon energy range 11–40 eV were taken with an electrostatic hemispherical analyzer using p -polarized light. The total energy resolution was ≤ 0.2 eV and the angular resolution was $\leq 1^\circ$. The incidence angle with respect to the surface normal was 45° . AIPES and Si L -edge XAS measurements were performed using the SOR ring at the Synchrotron Radiation Laboratory of the Institute for Solid State Physics, University of Tokyo. The valence spectra were taken with a double cylindrical mirror analyzer. The total energy resolutions were 0.43 and 0.05 eV for the valence and the XAS spectra, respectively.

Si L_{III} -edge XAS ($2p_{3/2}$ to conduction bands) spectra and valence spectra obtained from a clean Si(001) surface (crystalline Si, c -Si) and a PS sample formed with a 4.5–6.0 Ω cm substrate are shown in Fig. 1. The binding energies of all of the spectra are with respect to the Si $2p_{3/2}$

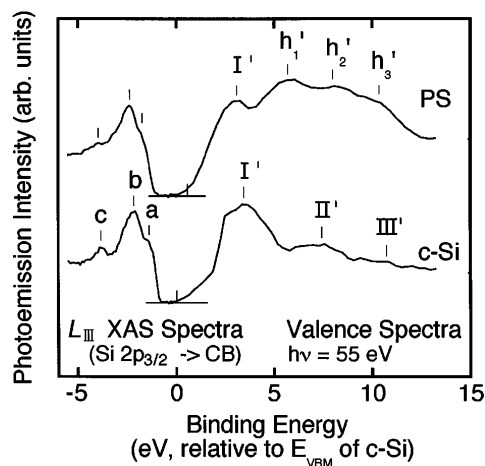


FIG. 1. Si L_{III} -edge XAS ($2p_{3/2}$ to conduction bands) spectra and valence spectra obtained from a clean Si(001) surface and a porous Si sample formed with a 4.5–6.0 Ω cm substrate.

core state and the value of the binding energy is indicated with respect to the valence band maximum (E_{VBM}) of the Si(001) surface. The E_{VBM} position is determined from the leading edge of the valence spectrum. To obtain the Si $2p_{3/2}$ core and the L_{III} -edge XAS spectra, measured spectra were decomposed into the Si $2p_{1/2}$ and Si $2p_{3/2}$ spin-orbit partner components using a spin-orbit splitting of 0.61 eV and a $2p_{1/2}$ to $2p_{3/2}$ intensity ratio of 1:2 [10]. The conduction band minimum (E_{CBM}) is determined by the onset of the L_{III} -edge absorption corresponding to the point of maximum slope [10]. The XAS and valence spectra from PS on a 0.01–0.02 Ω cm substrate were similar to those for the PS on a 4.5–6.0 Ω cm substrate. In the L_{III} -edge XAS spectrum of the clean Si(001) sample, three features, denoted by a , b , and c , are observed. The features have been previously identified with transition to maxima in the density of conduction states; X_1 , L_1 , and L_3 , respectively [10]. These critical points are absent completely in the XAS spectra of both amorphous Si (a -Si) and hydrogenated amorphous Si (a -Si:H) [11]. However, in the PS spectrum, these critical points are still clearly observed, indicating that Si crystallinity is retained in PS.

In the valence spectrum of the Si(001) surface, three well-known peaks, denoted by I' , II' , and III' , are observed, which are attributed to the X_4 , L_1 , and L_2' symmetry points, respectively [12]. In the valence spectrum of the PS sample, the I' feature and three weak peaks, denoted by h'_1 , h'_2 , and h'_3 , are observed. We have assigned previously the three weak peaks to the characteristics states induced by both monohydride and dihydride configurations on the PS surface [7,8]. No oxygen-related feature has been found on both the valence and XAS spectra. The results of our previous Auger electron spectroscopy studies also do not indicate any oxygen trace on the as-anodized PS surface [8]. Thus, the as-anodized PS surface is basically covered with hydrogen. The I' peak is also observed from a -Si [13]. The feature originates from the p -derived states and is less sensitive to the long-range order than the

II' and III' features [14]. Upon hydrogen chemisorption, the valence spectra of both crystalline and noncrystalline Si exhibit the I' peak, and their hydrogen-induced states and spectral shapes are similar to each other [15,16]. Thus, it is generally difficult to judge the change in the bulk structure from the valence spectra. However, the conduction states are much more susceptible to the absence of long-range order as seen in the L -edge XAS spectra.

The E_{CBM} and E_{VBM} positions of the PS sample with respect to those of crystalline Si shift toward a higher potential by ~ 0.35 eV and toward a lower potential by ~ 0.55 eV, respectively, resulting in the band gap widening by ~ 0.9 eV, as shown in Fig. 1. The ratio of the E_{CBM} and E_{VBM} shifts is in good agreement with the other reported ratio ($\sim 1:2$) [17]. The I' peak position of PS is almost unchanged with respect to that of c -Si. Thus, the shift in the E_{VBM} position results from a steepening of the leading edge induced by the recession of the topmost valence states. This E_{VBM} recession is also observed in a -Si:H; however, the E_{CBM} edge does not shift with respect to that of crystalline Si [18]. The stationary E_{CBM} edge and receding E_{VBM} edge phenomena have been explained as being due to the lower self-energy of the $H(1s)$ orbital with respect to the $Si(sp^3)$ hybrid which compensates the shift in the E_{CBM} edge [19]. Thus, the band edge behavior of PS is in contrast to the case of the noncrystalline modifications.

Figure 2 shows normal emission spectra obtained from PS samples formed with 0.01–0.02 and 4.5–6.0 Ω cm substrates. The binding energies of the spectra are with respect to the E_{VBM} leading edge of the spectrum taken with $h\nu = 40$ eV. For such a high photon energy, the normal emission spectrum reflects the density of states [20].

The spectra obtained from the samples formed with substrates of two different resistivities are very similar to each other. In these spectra, some broad features with large background contributions are observed. However, their dispersive and nondispersive structures can be clearly identified. The spectra show a dispersive peak, denoted by C' , for $h\nu = 11$ and $12\sim 15$ eV; a nondispersive peak, denoted by E' , at ~ 3.2 eV for $h\nu = \sim 16\sim 18$ eV; and a dispersive peak, denoted by H' , for $h\nu = 20$ and 22 eV. For $h\nu = 32$ eV, one large feature centered at ~ 2.5 eV, denoted by A' , is observed. Several weak features are seen in the lower binding energy side of peaks C' and E' . However, their energy positions are not clearly determined. In the higher binding energy side of the spectra, two large nondispersive peaks, denoted by h_1 and h_2 , are observed. The nondispersive h_1 and h_2 peaks are located at almost the same energy positions as the h'_1 and h'_2 peaks in the PS valence spectrum. Thus, the h_1 and h_2 peaks correspond to the h'_1 and h'_2 peaks and originate from the hydrogen-induced states.

These spectral features are compared with those obtained from crystalline Si surfaces. Johansson *et al.* [21] have reported recently on the precise normal emission

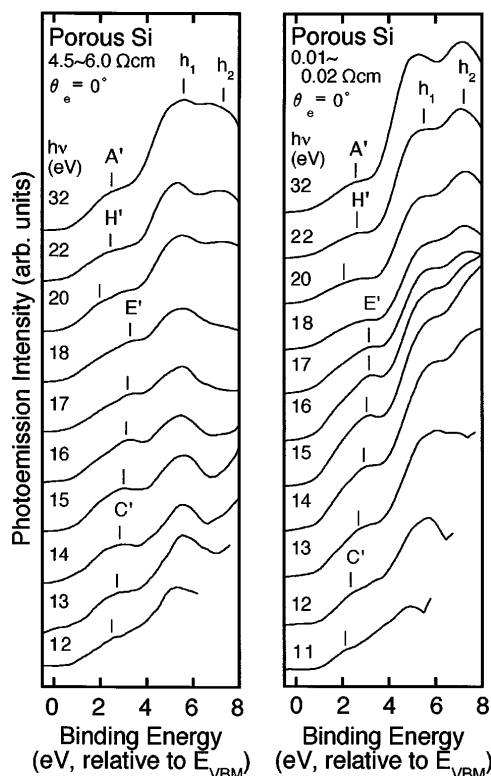


FIG. 2. Angle-resolved normal emission spectra along the Γ - Δ - X symmetry line obtained from porous Si samples formed with 0.01–0.02 and 4.5–6.0 Ω cm substrates.

study on a clean Si(001) 2×1 surface using p -polarized light. The spectra taken for an incidence angle of 45° , which is the same angle as that used in this study, show a dispersive structure denoted by C for $h\nu = 11$ –15 eV, a nondispersive structure denoted by E at ~ 3.1 eV for $h\nu = 17$ –26 eV, a dispersive structure denoted by H for $h\nu = 17$ –30 eV, and a nondispersive peak denoted by I at ~ 1.5 eV for $h\nu = 13$ –16 and 21–26 eV. For $h\nu = 30$ eV, one large broad feature (denoted by A in this paper) is observed at ~ 2.5 eV. It is found clearly from the spectra that peak A is not related to peak H and merges with peaks I and E . The other feature is a nondispersive peak denoted by S , which is very close to E_{VBM} . The dispersive peaks C and H and the nondispersive peak E have been identified as the direct transitions from Δ_5 to Δ'_2 bands and from Δ'_2 to Δ'_2 bands and the nondirect transition from a high DOS region near the X_4 symmetry point, respectively. The I peak has been interpreted as being related to the surface-umklapp scattered transition from the high DOS region near the L'_3 symmetry point. The S peak is the well-known surface state associated with the dangling bonds on the 2×1 reconstructed surface [22].

The C , E , H , and A bulk features appear in the normal emission spectra of the PS samples for almost the same photon energy range and their binding energy positions correspond well with those of the C' , E' , H' , and A' features. These facts are consistent with the preservation of the crystalline Si bulk features in the XAS spectra of the PS sample. In the spectra of the clean Si(001)

surface, the h_1 and h_2 peaks are not observed; on the other hand, the E peak is observed up to $h\nu = 26$ eV. However, the corresponding E' peak in the PS spectra is not confirmed above $h\nu = \sim 20$ eV. The obscurity of the E' feature above $h\nu = \sim 20$ eV is probably due to its merging with the large contribution of the lower energy side of the h_1 peak. The energy positions of the weak features seen in the lower energy side of the peak C' are not clearly determined; however, they are close to that of the I feature, suggesting that similar surface-umklapp scattered transitions may also be involved for PS. The S peak is not seen in the PS spectra. Since the hydrogen termination is known to eliminate the surface states of a clean surface [22], the lack of the dangling bond S states is due probably to this hydrogen termination.

Nondispersive bulk features are often referred to as the nondirect transitions from high DOS regions. The binding energy of the nondispersive E' peak (~ 3.2 eV) agrees well with that of the nondispersive E peak (~ 3.1 eV) in the spectra of the Si(001) 2×1 surface and is also close to the theoretically obtained value (2.8 eV [21], 3.1 eV [23]) for X_4 . Thus, the E' peak is assumed to be due to the transition from the flat band region near the X_4 symmetry point. Using the direct transition model, the final bands of the transitions corresponding to the dispersive C' and H' peaks are mapped with the theoretical band structure along the Γ - Δ - X symmetry line calculated by Johansson *et al.* [21]. To obtain the final states, the initial states are determined first by fitting the binding energy positions of the C' and H' peaks to the calculated valence bands. In the analysis, the band energies of the top valence bands have been multiplied by a constant factor so that it reproduces the experimentally obtained energy 3.2 eV for X_4 , and this procedure has been applied to the mapping analysis for the Si(001) surface [21]. The results are shown in Fig. 3. For the C' peak, the C' - E' peaks seen for $h\nu = 11$ and 12–17 eV are mapped. The C' and H' peaks are identified as the transitions from VB3,4(Δ_5) to CB10(Δ'_2) and from VB2(Δ'_2) to CB15(Δ'_2), respectively. Both of the transitions are dipole allowed for the polarization vector used in this work [24]. In the case of the Si(001) 2×1 surface, only two transitions are observed for $h\nu \geq 11$ eV as direct transitions and are similar to those described above [21]. Therefore, all of the direct transitions as observed from a clean Si(001) are reproduced for photoluminescent PS. Above $h\nu = \sim 16$ eV, the mapping points near CB10 deviate slightly from those at CB10. This is because, at higher photon energies, the corresponding transitions exhibit the nondirect transition character, the E' feature.

The L -edge XAS and ARPES studies reveal that, even if PS is photoluminescent enough to be observed by the naked eye, it still possesses the crystalline symmetry of bulk crystalline Si. The fact suggests that the clear p -derived peak in the top valence band reflects the X symmetry to some extent. Since the detection depth for the normal emission for $h\nu = 11$ –30 eV is estimated to

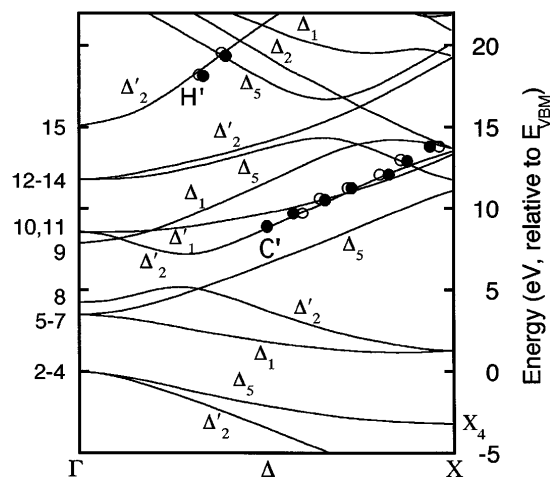


FIG. 3. Theoretical band structure of Si along the Γ - Δ -X symmetry line calculated by Johansson *et al.* [21]. Experimental direct transitions from VB 2 (denoted by H') and VB 3,4 (denoted by C') are shown with open and closed circles for porous Si samples formed with a 0.01–0.02 and a 4.5–6.0 Ω cm substrate, respectively.

be 5–13 Å [25], the presence of the electronic structure of bulk crystalline Si is contradictory to the uniform formation of noncrystalline materials or other Si networks different from the bulk crystalline Si. Although the recession of the top valence band is observed and the E_{VBM} edge shift is measured using the leading edge, a small amount of tail still remains near the E_{VBM} position as shown in Fig. 1. These results probably result from the overlap of the valence structure of bulk crystalline Si and the receding valence structure. This suggests that the bulk crystalline Si states affect the determination of the band gap for the receding valence structure. However, we have reported previously that the surface band gaps of PS determined with the same method as that presented here are well related to the PL peak energy [8]. This fact indicates that the measured band gap and then some local parts having the receding valence structure may be related to the luminescence origin. It is noted that the results of the PS band edge behavior again exclude the localized formation of noncrystalline structures. Both the PS samples formed with a 0.01–0.02 and a 4.5–6.0 Ω cm substrate still have the bulk Si band structures and their structures are almost the same. Thus, the bulk Si electronic structure which is partly present in PS is not affected by the change in microstructure and porosity of PS. This also implies that the nonbulk crystalline structures, which are also present, do not affect the electronic states of the bulk Si structure significantly. Very localized microstructures which are formed on bulk crystalline Si are likely to be the luminescence-related structures. Considering the earlier reported optical and electronic properties of PS, which can be explained partly by the bulk size effect [8,17], we believe that the microstructures contain quantum-sized structures.

We greatly acknowledge the support by the staff of the Synchrotron Radiation Laboratory of the Institute for

Solid State Physics, University of Tokyo, and by the staff of the Photon Factory at the National Laboratory for High Energy Physics. This work is supported in part by a Grant-in-Aid from the Ministry of Education, Sports, Science, and Culture of Japan, and the Research Foundation for Opto-Science and Technology.

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