

Electronic signature of the pentagonal rings in silicon clathrate phases: Comparison with cluster-assembled films

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The valence-band spectrum of the silicon Si-34 clathrate phase has been measured by photoemission spectroscopy. In contrast with tetrahedral Si (diamond phase), the clathrate structure presents mainly five-member rings. From the comparison between the tetrahedral Si and the clathrate spectra, we show that the presence of odd-member rings induces the merging between *s*-like and *sp*-like bands and a strong reduction of the valence-band width. These results are corroborated by first-principles calculations within an accurate quasiparticle approach. [S0163-1829(98)05240-0]

During the last three decades, a considerable effort has been devoted to the understanding of the polymorphism of silicon (Si) with particular attention to the *sp*³-hybridized networks.¹⁻⁵ For example, the presence of topological defects, as compared to the “ideal” *sp*³ diamond structure (*c*-Si), is of much importance since it is expected to greatly influence the structural, dynamical, and electronic properties of various Si-based materials such as (e.g.) amorphous silicon (*a*-Si), cluster-assembled films, reconstructed surfaces or interfaces, and *c*-Si core dislocations.⁶ Since the early work by Joannopoulos and Cohen,¹ it has been suggested¹⁻⁴ on theoretical grounds that the presence of pentagons significantly affects the valence-band (VB) density of states (DOS) and the fundamental band gap. However, on the experimental side, measurements conducted on the various phases quoted above average over both the even- and odd-member rings and it is difficult to resolve each contribution specifically.

New crystalline phases named clathrates,⁷ which are built from the regular arrangement of a combination of Si₂₀ (*I_h*) and Si₂₄ (*D_{6d}*) or Si₂₈ (*T_d*) cages, have been synthesized. Both the crystalline order and the very large predominance of fivefold rings (87%) in such materials should allow one in principle to specifically study the signature of the odd-member rings and much theoretical effort has been recently devoted to the study of the electronic properties^{8,9} and phonon modes¹⁰⁻¹² of such materials. In this work, we report on a measurement of the VB DOS of a clathrate on the basis of photoemission spectroscopy (XPS). Our results clearly show that the presence of pentagons induces a contraction of the VB width and the merging of the *s* and *sp* occupied subbands with respect to tetrahedral Si. These results are corroborated by *ab initio* calculations within an accurate quasiparticle approach.

Our clathrate samples (labeled Si-34) can be described as being composed of Si₂₈ face-sharing polyhedra, with a Si atom in the vertices (space group *Fd3m* *a* = 1.462 nm). The space between the Si₂₈ forms Si₂₀ cages and each atom is in

a *sp*³-like configuration. The samples used for this study were obtained by thermal decomposition of NaSi under vacuum (10⁻⁶ Torr) in the temperature range 670–710 K. They are in the form of a powder with a mean grain size of the order of a few micrometers. The crystalline phase purity was deduced from the x-ray diffraction pattern. A small sodium component remains within the cages. In order to check its influence, we have studied two stoichiometric compounds Na_{*x*}Si-34 with respectively *x* = 7 (labeled clat1) and *x* = 1 (labeled clat2). A careful analysis of the x-ray powder diffraction pattern reveals that the alkali atoms occupy preferentially the Si₂₈ cages. Therefore, in the clat1 phase, all the Si₂₈ cages are endohedrally doped. We find that the VB of both the clat1 and clat2 samples are very similar, yielding DOS peaks at the same energies.

Clathrates samples are introduced in a dual XPS/Auger camera Nanoscan-100 type microprobe operating at a base pressure < 4 × 10⁻¹⁰ Torr. The XPS is performed using Al K_α x-rays (1486.6 eV).¹³ The clathrate samples were compared to a nearly intrinsic Si(100) crystal (*ρ* < 400 Ω cm, *n*-type, at room temperature, labeled tetrahedral Si). The most accurate VB is obtained by *in situ* crystal cleaving before analysis. In our case, such a procedure is of course possible for the reference sample but unsuitable for the clathrate powders, which are therefore previously pasted on another Si substrate. Both samples are cleaned by chemical way (HF solution) and dried by a N₂ gas just before introducing them into the XPS apparatus. To check the influence of the “glue,” we have compared the spectra obtained for the clathrate powders pasted or directly deposited on a gallium or indium substrate. The differential charging was estimated to be ~0.2 eV (because of the insulating character of the glue). This value sets the accuracy of our data.

Figure 1 shows the XPS near the Fermi level observed for the reference (a) and the clat1 (b) samples. These spectra are corrected for the inelastic scattering tail. The Si_{2*p*} core line is taken as a reference to align the (a) and (b) spectra.¹⁴ We observe in both cases three “subbands,” well known in the

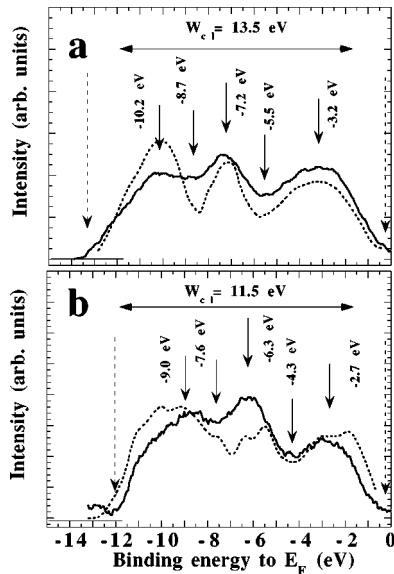


FIG. 1. VB DOS for tetrahedral Si (a) and clathrate (b). The dotted and continuous lines are, respectively, the theoretical and experimental spectra. The theoretical spectra are calculated from the DOS (Fig. 2) after several corrections indicated in the text. Theoretical and experimental spectra have been aligned through matching of the intrinsic Fermi level.

case of tetrahedral Si, and that we label respectively s , sp , and p with respect to their angular momentum character.¹ We find, however, significant differences in the position and width of these subbands when comparing both phases. In particular, the clat1 total VB width ($W_{c1}=11.5$ eV) is smaller than the tetrahedral Si one ($W_d=13.5$ eV). Further, the clat 1 s subband maximum lends at roughly the same energy as the “valley” between the s and sp subbands of tetrahedral Si. These measurements confirm therefore on an experimental basis that the presence of pentagonal rings significantly affect the VB electronic DOS and the corresponding modifications are clearly identified.

Further insight into the properties of the pentagonal rings may be obtained by conducting a first-principles study of the electronic DOS of Si-34. The present calculations are first performed within the local density approximation¹⁵ (LDA) to the density functional theory (DFT).¹⁶ A standard pseudopotential¹⁷ is used for Si and the wave functions are expanded on a plane-wave basis with kinetic energy up to 20 Ry. We first relax the system with respect to both cell size and atomic positions and find a lattice constant of 27.55 a.u. We then calculate the band structure of Si-34. The VB width and fundamental band gap are, respectively, 10.84 and 1.25 eV. This can be compared to 11.92 and 0.51 eV for bulk Si within the same theoretical framework. Therefore, the band gap opens by 0.7 eV from the tetrahedral Si to the clathrate phase, in good agreement with the results of Refs. 8 and 9, while on the contrary the valence-band width decreases by 1.1 eV.¹⁸

We recall now that the DFT usually underestimates by as much as 50% the band gap of semiconductors and insulators. In order to provide an accurate value for the band gap of Si-34, we perform further a quasiparticle energy calculation¹⁹ for both the tetrahedral Si and clathrate phases. We find that within this formalism, the band gap of both the

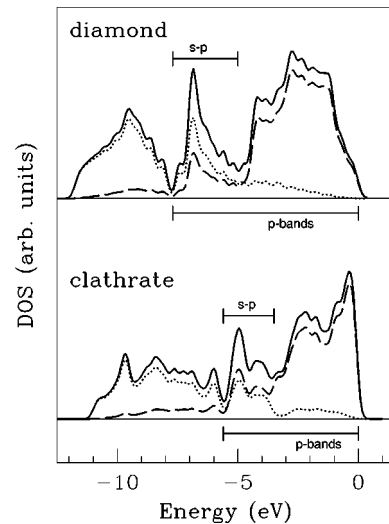


FIG. 2. Theoretical DOS for tetrahedral Si and Si-34 (solid lines). The s - and p -resolved contributions are shown with dotted and dashed lines, respectively. The angular momentum decomposition of the DOS is obtained by projecting the wave functions on a spherical harmonics basis centered on each Si atom. The DOS have been aligned at the VB top edge. A 0.1-eV Gaussian broadening has been used.

clathrate and c -Si phases opens up to 1.9 and 1.2 eV, respectively. As for the VB, the effect of the quasiparticle correction as compared to DFT-LDA results merely in a slight “stretching” of the VB width, which increases by ~ 0.25 eV in both cases. The resulting DOS are represented in Fig. 2 and compared to the experimental data in Fig. 1. In this latter case, the effect of cross-section modulation for $3s$ and $3p$ states and a broadening taking into account the experimental dispersion have been applied for better comparison with the experimental results.²⁰

We further plot in Fig. 2 the s -resolved (dotted line) and p -resolved (dashed line) DOS. The calculated DOS reproduce quite well the experimental observations, namely, the shift of the s and sp bands and the reduction of the VB width in the clat1 phase as compared to tetrahedral Si. We do not observe a clear reduction of the s -DOS band width but rather a loss of structure. On the contrary, the band width of the p -DOS decreases by ~ 2 eV from the tetrahedral Si to the clathrate phase. This strong reduction, which affects the top of the VB, can clearly explain both the ~ 0.7 -eV opening of the band gap and the ~ 1 -eV shift towards the Fermi level of the sp peak in the Si-34 phase as compared to the tetrahedral Si reference. As another consequence, we observe a strong “steepening” of the DOS just below the top of the VB edge in the clathrate phase as compared to tetrahedral Si. This is very similar to what happens in a -Si for which one would expect the introduction of random disorder to broaden the bands.

Now, we can use the clathrate sample as a reference to study other Si phases such as cluster-films.²¹ Figure 3(a) shows the “addition” of both the tetrahedral Si and clathrate sample’s XPS spectra. This is compared in Fig. 3(b) to the XPS of a film obtained by the deposition of free Si (size range 20–50 atoms).²¹ Such small clusters present a combination of fivefold and sixfold rings. The straightforward addition of both the tetrahedral Si and clathrate sample’s XPS

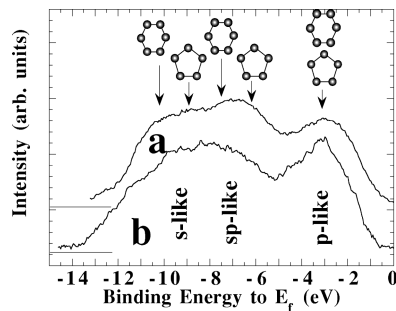


FIG. 3. Addition (1/1 ratio) of both the experimental VB of the clathrate and Si-diamond samples (a) compared to the VB observed for cluster-assembled films (b) (see Ref. 21). The corresponding “ring configurations” are given at the top of the figure.

spectra is certainly a rather crude approximation that should not be used to describe the fine details of Fig. 3(b). However, one observe in both cases a large merging of the s and the sp bands as mentioned for other structures such as a -Si (Ref. 22) or porous silicon.²³ As emphasized above (see Fig. 1), this feature originates in the shift of the s -pentagon-related band as compared to the bulk diamond structure. It appears therefore that the s - and sp -like bands merging is the signature of the fivefold rings, as originally proposed by Joannopoulos and Cohen¹ on the basis of calculations performed on the hypothetical ST-12 Si phase. The present experimental results clearly confirm these early predictions. Let us emphasize that the filling of the valley between both s - and sp -like bands is achieved with a large proportion of five-member rings [43% in Fig. 3(a)]. This is a confirmation of the so-called memory effect in cluster-assembled films, namely, that such materials “remember” the structural properties of the corresponding free clusters.²⁴

Finally, we report on the XPS spectra obtained after *in situ* bombardment by Ar^+ ions. Figure 4 gives the resulting VB DOS for the tetrahedral Si reference (a) and the clatI (b) samples. The spectra, which both show a strong modification as compared to Figs. 1(a) and 1(b), are now remarkably similar, indicating that both samples have transformed into a similar structure under bombardment. This suggests that the defects in clathrate are formed by even-membered rings such as Si_6 while those in diamond phase are constituted by odd-membered rings such as Si_5 . In this respect, the two struc-

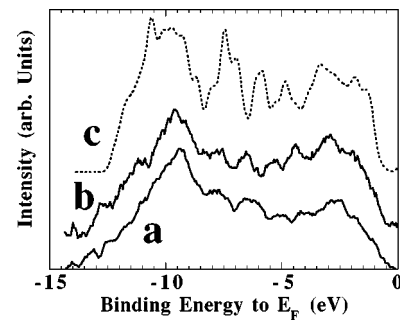


FIG. 4. Valence band for Si diamond (a), and clathrate (b) after Ar^+ etching. The addition of the clathrate and Si-diamond theoretical DOS in a 1/1 ratio is shown in (c). In this latter case, the intrinsic Fermi levels have been aligned and the s and p cross-section corrections have been applied as in Fig. 1.

tures are “dual” if we consider the nature of the defects selectively created during the etching process.²⁵ The similarity between both spectra and their stability under further bombardment suggests that in both cases the number of odd- and even-membered rings is comparable.²⁶ Such dual defects yield electronic levels in the valley between the s and sp bands, leading again to their merging. This is another experimental confirmation that the merging between the s and sp subbands originates in the coexistence of odd- and even-membered rings in a close to 1/1 ratio.

In conclusion, we have studied both theoretically and experimentally the valence band spectrum of a pure Si crystalline clathrate phase having mainly pentagonal rings. The position of the subbands attributed to such odd-membered rings has been measured. By comparison with the valence-band spectrum of tetrahedral Si, we have shown that the introduction of pentagons in the diamond lattice leads to a merging of the s - and sp -like bands, the contraction of the VB width and to a steepening of the DOS below the VB edge. The availability of precise and specific data for pentagonal rings should prove very useful to further study various Si structures such as (e.g.) a -Si, cluster-assembled films, reconstructed surfaces, and interfaces or core dislocations in solids.

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¹³The resolution was measured at 1.2 eV on Ag $3d_{3/2}$ line for the

core levels. For the VB measurements the energy pass was fixed at 0.8 eV. For depth profile, we use an argon ion operating at low flux ($<10^{-8}$ Torr) and medium energy (3 keV). The etching rate is less than a few monolayers per hour.

¹⁴This procedure of alignment through calculation of the Si_{2p} core lines is necessary in the present case since the position of the Fermi level is unknown for the clat1 sample. For both the tetrahedral Si- and clat1 samples, the Si_{2p} core level were measured to be equal within the 0.2 eV accuracy of our measurements. This indicates that the possible core-level shift between both phases is rather small. We note that the position of the Si_{2p} line with respect to the intrinsic Si-diamond Fermi level is equal to 99.3 eV.

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bottom of the conduction bands, leaving the VB unchanged, in good agreement with previous theoretical work (Refs. 8 and 9) and with the present conclusions drawn from the comparison of the clat1 and clat2 spectra.

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