Ab-initio Calculation of Si–K and Si–L ELNES Edges in an Extended Inactive Defect Model of Crystalline Silicon

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The Si–K and Si–L2,3 edges of the electron energy-loss near-edge (ELNES) spectra of a model of an extended inactive defect in Si with no dangling bonds were calculated using an ab-initio method which includes the electron-hole interaction. In this method, atom-by-atom excitation is possible. The calculated results are discussed in the context of the subtle structural differences in the local atomic environment. Comparison of the results with measured data shows satisfactory agreement. The method can be applied to other more complicated defective systems such as grain boundaries and interfaces for effective materials characterization.

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1. Introduction

Defects play a crucial role in all semiconductor and ceramic devices. Active defects such as vacancies and impurities dramatically change materials properties and affect the device performance. On the other hand, the influence of inactive defects can be more subtle, since the deviation from the perfect crystal structure of passive defects is usually not large and changes in the electronic properties are minimal.

Electron energy-loss spectroscopy (EELS) is an important experimental probe for materials research. 1) In particular, the electron energy-loss near edge spectroscopy (ELNES), in conjunction with high-resolution transmission electron microscopy (HRTEM) is a very effective tool to study the structure and bonding of materials and their defective structures. The interpretation of the measured ELNES spectra has never been an easy task. Reliable theoretical calculations can be very helpful and should be a standard part of data analysis. Although considerable progress has been made in the electronic structure theory related to ELNES interpretation within the last decade, 2,3) excellent agreements between the calculated and measured ELNES spectra of many simple crystals remain elusive. A traditional approach to the interpretation of ELNES data is to use the local density of states (LDOS) of the conduction band (CB) obtained from a ground state electronic structure calculation. On the basis of the dipole selection rule and by neglecting the transition matrix elements, the K and L edges of the ELNES spectra can be reasonably represented by the p- and (s + d) components of the LDOS respectively. There were many instances that the LDOS approach has only very limited success in crystalline systems. 4–7) Very often, one managed to obtain a satisfactory agreement for one edge but failed miserably for other edges in the same crystal. So, unless a calculation can reproduce the well-known spectra of simple crystals, its application to defective systems will not be reliable.

Recently, we have developed a rigorous ab-initio method for ELNES calculations, 8) which includes the electron-core-hole interaction. Application of this method to several oxides and nitrides including α-Al2O3, MgO, MgAl2O4, 7) α-Si3N4, β-Si3N4, Si2N2O, 9) α-SiO2, stishovite SiO2, 10) and Y3Al5O12 (YAG), 11) all are in superior agreements with the measured spectra. A common feature in these studies is that all edges for all atoms in the crystals were calculated, (e.g., the cation K and L-edges and the anion K-edges,) not just a selective edge for a specific ion. Comparison with available experimental data shows excellent agreements in peak positions, peak shapes, relative intensities, and even smaller structures in almost all cases.

In this paper, we report the results of the application of this method to an extended defect model of crystalline Si. The Si–K and Si–L2,3 edges of a selected number of Si atoms with different local distortions have been calculated and compared. We further discuss the potential application of this method to other structurally complicated systems such as grain boundaries (GB) and interfaces.

2. Description of the Model

A nanoscale extended defect structure in crystalline Si is formed by electron or ion irradiation. This {113} extended defect is planar or rod-like agglomerates of self-interstitials, and has serious effects on dopant diffusion in si-based devices. It is well known that the basic structure of this defect has no dangling bonds, 12) and thus this defect is basically inactive without any gap states. 13) However, the presence of the bond disorder and the topological disorder should make substantial effects on the electronic structure, which is quite exciting to study both experimentally and theoretically.

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3. Method of Calculation

Based on the HRTEM image of the defect sample, a supercell structural model of the [113] defect was constructed and fully relaxed by the ab-initio pseudopotential method. The periodic supercell model contains 90 Si atoms with primitive lattice vectors of \( R_1 = (\sqrt{22}/2)a_0\bar{e}_{32}, R_2 = (\sqrt{2}/2)a_0\bar{e}_{110}, R_0 = 2\sqrt{11}a_0\bar{e}_{113} + 0.032^* (\sqrt{38})^* a_0\bar{e}_{116} \). Figure 1 shows the defect model viewed in the ⟨110⟩ direction. All the 90 atoms in the supercell are numerically labeled for easy identification. The 90-atom model with periodic boundary condition can be roughly divided into two regions, a defective core region which contains only 6-membered rings as in the crystalline case such that each Si atom is in an ideal tetrahedral bonding configuration. Electronic structure calculation shows only a little difference in the DOS of Si atoms in the defective core region and those in the bulk-like region. Transmission EELS spectroscopy was able to show a very small shift in the Si–L edge between the spectrum obtained from the defective model and those in the bulk region.

The ELNES spectra (Si–K and Si–L 2p edges) of the atoms in the above defect model were calculated by the ab-initio method which is based on the orthogonalized linear combination of atomic orbital (OLCAO) method. The OLCAO method is a density-functional-theory-based electronic structure method particularly suitable for large complex systems. Detailed description of the computational procedures for the ELNES calculation has been described elsewhere. In the present calculation, the defect model itself serves as a supercell and the ELNES spectra for any atom can be obtained. First, the ground state electronic structure is calculated using the ab-initio OLCAO method. One of the Si atoms in the model is identified as a target atom in which the core orbitals are retained in the basis set, while those of all other Si atoms are eliminated by orthogonalization to reduce the dimension of the secular equation. The core state (Si-1s for the K-edge and Si-2p for the L-edge) of the target atom in the ground state provides the initial state in the ELNES spectral calculation. The final states are the CB states calculated separately. An electron in the specified core level of the target atom is “excited” to the lowest CB, leaving a hole behind. The interaction and the screening of the hole and the electron in the CB are accounted for by the self-consistent iterations of the standard Kohn-Sham equation until the potential converges. The final states thus obtained are distinctively different from the CB states from the ground state calculation, which contain no electron-hole interaction. The ELNES edge is obtained by evaluating the transition spectra from the initial state to the final states. The inclusion of matrix elements of transition in the calculation automatically imposes the dipole selection rule. The calculation is repeated for different target atoms in the defective model so that the spectral differences related to the topological disorder can be ascertained.

The ab-initio calculation provides the total energies (TE) for both the initial ground state and the final core-hole state. Their difference can be related to the transition energy at the edge onset. This makes the comparison between the measured and the calculated spectra more meaningful. In the LDOS approach, one simply aligns the main peak in the calculated and measured spectra. This could sometimes lead to wrong assignment if the spectrum has multiple structures. In the present study, the onsets of the Si edge for different Si atoms are slightly different because of the minor deviations in the local bonding structure. Such differences are reflected in our calculation through the difference in the total energies.

To correlate the calculated ELNES spectra with the local structural differences of the Si atoms in the model, we have analyzed the bond angle (BA) and bond length (BL) distor-
tions in the model. We have also calculated the bond order (BO) (also called overlap populations) between every Si–Si nearest neighbor (NN) pairs using the ground state wave functions and the Mulliken scheme.\textsuperscript{17} The BO is a measure of the bond strength between a pair of atoms. It generally scales with the bond length but also depends on the overall local structural environment. To put it succinctly, the BO reflects the effects of both the BL and BA distortions in the model. For each Si atom, there are four NN Si–Si bonds (therefore four BO values) and six Si–Si–Si tetrahedral angles. Figure 2 shows the standard deviations $\sigma$ of the BO, BA and BL for all the 90 Si atoms in the model. A large $\sigma$ implies a large local structural disorder for that atom. Figure 2 shows the largest deviations in BO, BA, and BL are from the following groups of atoms: Si1 to Si9, Si23 to Si31, Si59 to Si66, and Si80 to Si90. The rest of the atoms (Si10 to Si22, Si32 to Si58, and Si67 to Si79) have very small deviations in BO, BL and BA, and they belong to the bulk-like region in Fig. 1. Figure 2 also shows that atoms with the largest BO deviations do not always correspond with those with largest BA or BL deviations. Figure 2 only shows the short-range-order in the model and not the medium-range-order due to the presence of the odd-member rings.

4. Results

The calculated Si–K and Si–L\textsubscript{2,3} spectra for selected Si atoms labeled 23, 24, 27, 28, 31, 45, 63, 75, 76, 79, 80, 83, 84, 87, 88, are shown in Figs. 3 and 4 respectively. The gross features of the spectra are the same, but substantial deviations in the spectral details are found. To facilitate the analysis of these spectra, we divide these atoms into five groups: (a) Si atoms with the largest deviations in BO (Si23, Si27, Si24); (b) Si atoms with the largest deviations in BA (Si24, Si84, Si87), (c) Si atoms with the largest deviations in BL (Si23, Si28, Si87); (d) Si atoms in the bulk region (Si45, Si75, Si76, Si79); (e) Other Si atoms not in the above four groups (Si31, Si63, Si80, Si83, Si88). We can clearly make the following observations which apply to both the K and L edges: (1) There are significant differences between the spectra for Si in the defect core region and those in the bulk-like region. (2) While the spectra for atoms in the bulk region are almost identical, those belong to the defect core have different structures and shifts in peak positions. (3) It is interesting to note that Si79 which is located near the boundary of the bulk region and the defect-core region, has its spectra in Figs. 3(c) and 4(c) differ slightly from those of Si-45, Si-75, and Si-76 which are well within the bulk region. (4) For Si atoms in the defect core region, there is no obvious correlation with the BO, BA or BL deviations. In other words, there is no close resemblance for the spectra within each group of (a), (b), (c). This implies that each Si atom in the defect region has its own unique bonding environment, and this unique feature is manifested in the calculated ELNES spectra.

Let us now focus on the variations of the ELNES spectra among different Si atoms in the defect region. For Si–K edges, the differences are mostly in the energy range below 1870 eV, especially near the edge onset around 1855 eV. For the Si–L\textsubscript{2,3} edges, the main variations are from the peak feature near 114 eV and also those near the edge onset. There are also substantial deviations in the smaller structures in the energy range between the main peaks near 118 eV and 125.5 eV.
To get some idea on why the spectra of Si84, Si87 and Si28 are so different near the onset region, we note that the average BA and BL for all Si atoms in this model are 109.4° and 0.2324 nm respectively. Si87 has a very large BA of 122.2° while Si-84 has a very small BA of 91.9°. These two Si atoms are nearest neighbors to each other and both belong to a distorted 7-member ring (see Fig. 1). Also, we find that Si28 has a relatively short bond of 0.2289 nm and Si87 has two long bonds of 0.2352 nm. Thus, the difference in the ELNES spectra is the results of local BA and BL distortions, especially the BA. It may be possible to correlate the shifts and changes in the entire spectra from the bulk-like features to the specific BA and BL variations, however, no further attempts were made at this stage since it will require the spectral calculations of all the 90 Si atoms in the model. It is conceivable that there may be correlation between the calculated ELNES spectra and the medium-range-order which will require analysis of the spectra from all the atoms forming different 5-, 6-, 7-, and 8-member rings.

To compare the calculated results with the experimental data, we would first say that the calculated Si–K and Si–L\textsubscript{2,3} edges for atoms in the bulk region (Figs. 3(d) and 4(d)) are
close to those measured for perfect crystalline Si. \(^{18}\) In an earlier paper published by some of us, \(^{15}\) it was shown that there is a very small shift (\(< 0.5\) eV to lower energy) in the leading edge of the \(L_{2,3}\) spectra for data collected at the defect region relative to the data collected at the defect-free region. Such a shift was attributed to the presence of old-member rings. \(^{15}\) Figure 4 appears to show such a trend. Defective atoms such as Si87, Si27, Si24 and Si31 show a slight shift in the S-\(L_{2,3}\) edge onset towards the lower energy from those of Si76 and Si79. However, shifts in the opposite directions are also observed (Si84, Si63). Thus, what was experimentally observed is the averaged shift due to different Si atoms in the defect region and is quite small.

5. Discussion

The above results demonstrate the effectiveness of \textit{ab-initio} calculation in providing detailed theoretical ELNES spectra of extended defect structures in semiconductors. Such spectra are difficult to analyze without the careful theoretical calculation and appropriate modeling because of the passive nature of the defect. The key element in the present calculation is the inclusion of the electron-core-hole interaction in determining the wave functions of the final states. Separate calculations of the initial ground state and the final core-hole state, as well as a proper inclusion of the transition matrix elements are necessary. A critical message from these calculations is that the ELNES spectra of complex structures cannot be interpreted simply by the LDOS approach commonly used for crystals, or by considering the coordination numbers and the type of nearest neighbor atoms in the crystal. It is not possible to establish a general rule for the so-called “finger-prints” that would enable us to predict the ELNES spectra of a material with unknown structure or composition.

It should also be pointed out that the above results can be further improved by using a larger supercell. The present model with 90 atoms is in the form of a long and thin parallelepiped. The lattice constant in the \((110)\) direction is only 0.359 nm which is too small. So when a target atom is “excited” in the calculation, it sees its image in the adjacent cell also excited. This can induce considerable error since fictitious “defect”-“defect” interaction is included. This can be avoided by doubling the cell size in the \((110)\) direction at the expense of a much higher computational cost. We are currently improving the methodology of the present \textit{ab-initio} ELNES calculation such that the use of supercells with a size of up to 500 atoms is a realistic goal.

As mentioned in the introduction, material properties are controlled, to a large extent, by the presence of microstructures such as GB or interfaces. It is considered that the atomic and electronic structure of the \([113]\) defect has similar features to those of coincidence GB in Si. \(^{19}\) To properly understand the energetics of such microstructures in ceramics and semiconductors is one of the most outstanding problems in materials science. \(^{20}\) The structure, and sometimes the composition, at the GB or interface are not entirely known. Add to the complication, impurities may segregate to the grain boundaries and the characterization of such system could be extremely complicated. Encouraged by the results of the present paper, we feel that it would be possible to apply the present method for theoretical calculation of the ELNES spectra in such systems. The crucial link is the availability of appropriate structural models for GBs or interfaces. Once such a model becomes available, the ELNES spectra can be studied in detail by “exciting” the atoms one-by-one across the GB. The process mimics the experimental procedure\(^{21}\) of obtaining the loss spectrum by scanning across the GB except the theoretical spectra can provide much more detailed information with superior spectral resolution. A match in the calculated and measured spectra indicates the validation of the GB model constructed. This approach does have some limitations. The construction of large GB models is itself a monumental task. The quality of the final spectral calculation is directly linked to the quality of the model constructed. Furthermore, a realistic model is likely to have at least several hundred atoms in the supercell and the demand for computational resources could be substantial. However, this is not an insurmountable obstacle given the rapid advancement of computing technology and further improvements in computational methods for large-scale applications.

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