Measurement of the predicted asymmetric closing behaviour of the band gap of silicon using x-ray absorption and emission spectroscopy

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Abstract. We experimentally observe the theoretically anticipated but so far unverified asymmetric band gap closing for the prototypical semiconductor silicon from room temperature up to the melting point. The shift of the valence band maximum contributes more than 60\% to the band gap closing in comparison to the shift of the conduction band minimum. Since we determine the temperature-dependent band edge positions with x-ray absorption and x-ray emission spectroscopy, our analysis also includes electron–phonon coupling features and processes inherent to core-level spectroscopies, like the multi-electron screening response.

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1. Introduction

The physics of semiconductors is governed by their electronic band structure, where the band gap is the key property. It determines the electrical properties, successfully applied over decades in microelectronics. Furthermore, it is widely used as a model system for modern electronic structure tools, such as density functional theory, and for \textit{ab initio} simulations of the band structure. Nevertheless, the exact reproduction of the size of the band gap with \textit{ab initio} methods is challenging and can only be solved by including the effects of excited electrons and valence holes in the optical spectrum \cite{1}. Green’s function approach, evaluating electronic self-energies and lifetimes in a dressed state picture, has proven to be reasonably accurate \cite{2}. A similar technique can be used for the theoretical description of the influence of thermally excited nuclear vibrations, i.e. phonons, on the electronic states \cite{3}. In addition, statistical methods like molecular dynamics or path integral simulations are used to study the temperature dependence of the band gap \cite{4,5}.

Although very accurate calculations for the overall band gap shrinking with temperature have been published \cite{3,5,6} and experimentally verified \cite{7–9}, an asymmetry in the thermal evolution of the valence and conduction bands has only been considered theoretically \cite{10,11}, unverified by experiments. The reason is that the optical methods commonly used for band gap measurements determine energy differences between the valence and conduction bands, but fail to determine the absolute changes in energy of the valence band maximum (VBM) and the conduction band minimum (CBM) separately. In addition, the indirect band gap of silicon prohibits direct transitions between the VBM and CBM, allowing only phonon-assisted optical excitations, inherently coupling phononic features to the optical measurement process. Measurements disentangling both contributing band edges together with a theoretical treatment will provide insight into the basic nature of electron–phonon coupling and its direct effects on the electronic structure. For the silicon band gap, the theoretical treatment of Lautenschlager \textit{et al} \cite{11} combined with Cardona and Gopalan’s \cite{12} results predicts an asymmetry around 65\% due to a partial cancellation of the effects of acoustic and optical phonons only on the CBM energy.

In this work, we determine the temperature-dependent energetic positions of the valence and conduction bands in crystalline silicon separately. Our approach is to use the silicon 2p core level as a reference for the energy position of the CBM and VBM upon thermal excitation. Without explaining this here in detail, in our understanding the core level is thermally uninfluenced and therefore at a fixed energy. In particular, we use the soft x-ray photon-in/photon-out techniques x-ray absorption spectroscopy (XAS) in total fluorescence yield \cite{13} and x-ray...
emission spectroscopy (XES). We observe the theoretically anticipated asymmetric band gap closing, the phonon-induced line width broadening of the core-excited state [1] and we determine, in addition, the relaxation energy of the core excitonic state in crystalline silicon [14–16].

2. Experiment

We conducted the experiment in beamline UE52-PGM at BESSY II, Germany. At pressures below $10^{-9}$ mbar, we heated weakly B-doped Si (100) samples (specific resistivity $> 50 \ \Omega \ \text{cm}$) for several seconds above 1200 K to remove the surface oxide. Cleanliness was ensured by photoelectron spectroscopy. We recorded the spectra with a Scienta XES355 soft x-ray spectrometer [17]. The silicon sample was heated resistively and the temperature was recorded pyrometrically. For the XAS measurements in total fluorescence yield, we used the x-ray spectrometer in zeroth grating order. The excitation bandwidth was set to 40 meV, determining the resolution for XAS. To minimize self-absorption effects, near-normal incidence on the sample was chosen, while the detector was standing at 17° grazing to the surface. With this geometry we maximize bulk sensitivity in contrast to previous measurements [18]. The spectra have been flux-normalized. We performed XES with an incident photon energy of 117 eV, well above the silicon $L_2$- and $L_3$-edges and below the silicon $L_1$ edge. The x-ray spectrometer was operated with a 300 lines mm$^{-1}$ grating at a resolution in the XES measurements of 400 meV Gaussian width.

In figure 1(a), the principle of the experiment is summarized using a density of states (DOS) calculation$^6$ together with the experimental x-ray absorption and x-ray emission data in figures 1(b) and (c). X-ray absorption is a measure of the DOS of the conduction band as seen through the dipole selection rule (figure 1(b)). XES determines the partial valence band DOS through the dipole-allowed radiative decay of valence electrons into a core vacancy (figure 1(c)). Whereas optical absorption methods determine the width of the band gap, but cannot distinguish between the CBM and the VBM, we can extract their energetic positions from the XAS and XES spectral distributions individually. The reason is that the silicon 2p core level involved in XAS and XES is at an unaltered binding energy, which we can use as an energy reference. We measure the energetic position of the CBM and VBM as shown in the experimental data in figures 1(b) and (c).

3. The asymmetric closing behaviour

In XES, we observe, with increasing temperature, a shift of the spectral distribution towards higher photon energies. Since the XES spectral distribution is governed by the valence hole final state only, minor deviations from the ground state DOS appear. In XAS, we observe how the silicon $L_3$ edge, representing the CBM, shifts to lower photon energies and broadens with increasing temperature. According to the final state rule of x-ray spectroscopies [19–24], the XAS spectral distribution is governed by the core-excited final state, leading to significant,

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$^6$ We take the electronic structure calculations from the Japanese National Institute for Materials Science database (http://caldb.nims.go.jp). For XAS and XES at the Si 2p level, a superposition of 90% $s$- and 10% $p$- and negligible $d$-partial DOS reflects the electronic dipole selection rule and admixing of dipole forbidden contributions from inelastic processes.
but temperature independent, core-hole-induced relaxation in comparison to the electronic ground state, which our detailed analysis has to take into account. In the studied temperature region, the phonon numbers evolve nearly linearly with temperature. As the discussed shifts depend on phonon coupling, we expect a linear behaviour. For lower temperatures, the situation is different.

We can now quantify the temperature-dependent broadening and energetic shifts of our XAS data. The core exciton—a single state at a fixed energetic distance to the CBM—modifies the absorption cross section, exhibiting a sharp edge instead of the smooth onset of the conduction band DOS [16]. Therefore, we cannot fit with the calculated DOS, but take the first derivative of the XAS spectral distribution with respect to the incoming photon energy, shown in figure 2(a). The turning point of the edge and the edge width are expressed in the peak position and the full-width at half-maximum (FWHM) of this representation. With a Gaussian fit, we extract the FWHM (figure 2(b)). We additionally show the value of the natural lifetime broadening at 0 K temperature [25, 26]. In our data, the increase in broadening is smaller than evolutions reported in the literature from photoelectron measurements at lower
temperature dependences [25, 27]. We measure $1.35(4) \times 10^{-4}$ eV K$^{-1}$ instead of $2.20(30) \times 10^{-4}$ eV K$^{-1}$ [25], which we attribute to the inevitable surface contributions in photoelectron measurements. Since the phonon broadening is proportional to the phonon number in the sample, it follows the Bose–Einstein distribution function, which evolves linearly in the considered temperature region for typical phonon energies in silicon.

In figure 3(a), the temperature-dependent Si $L_3$ absorption edge position, taken from the peak in the first derivative, is shown. With increasing temperature it shifts linearly towards lower energies, representing the temperature dependence of the silicon CBM. In figure 3(a), we also show the temperature-dependent VBM as determined with XES. The analysis procedure we use here is to fit the measured XES data with the calculated DOS, convolved with the spin–orbit split Si 2p level (energy separation 0.6 eV, intensity ratio 2 : 1 [27]) and a Gaussian to mimic the experimental resolution, where only the energetic position and the total intensity are fitting.
Figure 3. (a) Position of the highest occupied states as measured with XES relative to the Si 2p core level and position of the Si \( L_3 \) absorption edge as a function of temperature. The red solid lines show linear fits. We show here all of the measured absorption edge positions, but have omitted some spectra in figures 1 and 2(a) for clarity reasons. (b) The measured difference in the CBM and VBM position as a function of temperature. The light-shaded region is the VBM contribution, the dark-shaded region reflects the CBM evolution. Both regions represent linear interpolations to the data. We also show the band gap as measured with optical methods [9]. The temperature-independent difference between both curves is due to the screening response in the core-excited state.

parameters\(^7\). Here, no excitonic features modify the spectral distribution and the measurement nicely represents the DOS in contrast to the XAS measurements. This justifies the different analysis procedures used.

We easily observe the asymmetry in the band gap closing, where the contribution from the VBM is much bigger. Fitting lines to the measured evolution, we calculate a slope

\(^7\) The given error of 70 meV is dominated by the error in the definition of the ratio of contributions from \( p \)- and \( s \)-states to the spectra. For a fixed ratio, the error averages to 10 meV. Different fixed ratios lead to temperature-independent offsets of the edge position. This analysis procedure is comparable to a deconvolution with the well-known detector response function; therefore the error can be much smaller than the spectrometer resolution.
of $+2.93(30)\times10^{-4}\text{ eV K}^{-1}$ at the VBM and $-1.61(5)\times10^{-4}\text{ eV K}^{-1}$ at the CBM. The mechanism influencing the thermal evolution of the electronic states is twofold. The indirect effect of lattice expansion due to the anharmonicity of the electronic potentials as a function of the interatomic distance and the direct coupling of phonons leading to renormalized electronic states both contribute to the shrinking of the gap \cite{7–12, 28, 29}.

Separating the VBM and CBM contributions, we find that the change in energy of the occupied states in the valence band due to thermal heating contributes 65% to the total band gap shrinking. For a comparison to theoretical predictions, we have to consider the work by Lautenschlager et al \cite{11} and the extension provided by Cardona and Gopalan \cite{12}. The earlier paper \cite{11} refers the energetic behaviour to an arbitrary reference level, appearing in their pseudopotential calculations. The later treatment \cite{12} analyses the temperature dependence of this reference level with respect to the thermally unaltered dielectric midgap energy, a concept introduced in \cite{30}. Combining both computations, the predicted asymmetry is around 64%, perfectly agreeing with our findings. Nevertheless, their estimated values for the total shrinking of the band gap are between 25 and 40% smaller than experimental values \cite{11}.

4. The multi-electron response in x-ray absorption

We then calculate the gap width as the difference between the measured CBM and VBM positions as shown in figure 3(b). Comparing our data to optical band gap measurements \cite{9}, the evolution with temperature agrees very well, but the absolute measured gap width is for temperatures up to 1400 K, constantly 0.37(2) eV smaller than determined with optical methods.

This is due to the multi-electron response in XAS forming a core exciton. To understand the local screening effects, we have to consider a total energy picture. The core hole appears as a net positive charge at the excited atom and thus influences the excited electron and the valence electrons. They rearrange to screen this charge, lowering the total energy of the system. Obeying energy conservation, the energy of the absorbed photon is given by the total energy of the final core-excited state (ground state energy set to zero) \cite{19–24}. Therefore, the edge energy does not reflect the single electron energy difference of the core level and the CBM, but is lowered by the collective screening response.

In XES, the final state is similar to optical spectroscopy, a valence hole, which is a small perturbation as compared to the core-excited XAS final state. So it lacks the multi-electron screening response to the core hole in XAS. This means that we can directly get the core excitonic screening energy ($E_{\text{screen}}$) from the difference between the Si $L_3$ edge energy as measured with XAS (CBM$_{\text{XAS}}$) and the VBM energy relative to the Si 2p level as measured with XES (VBM$_{\text{XES}}$), subtracted from the optically measured band gap ($(\text{CBM} - \text{VBM})_{\text{optical}}$)

$$E_{\text{screen}} = (\text{CBM} - \text{VBM})_{\text{optical}} - (\text{CBM}_{\text{XAS}} - \text{VBM}_{\text{XES}}).$$

Thus, the observed offset of 0.37(2) eV represents the temperature-independent lowering of the total energy due to the screening of the Si 2p core hole in XAS, cf the discussion in \cite{14–16}.

In figures 3(a) and (b), we further observe a deviation from the linear change in the XES data at 1550 K. The VBM as measured with XES seems not to shift anymore. At this temperature the gap between CBM$_{\text{XAS}}$ and VBM$_{\text{XES}}$ is very small. At the atomic site with the core hole, present for around 8 fs \cite{25} in the intermediate state of XES, the electronic band structure is locally distorted due to the apparent positive charge, with a localized change in energy of the order of the screening energy. So not only valence band electrons rearrange to screen this charge,
but also tunnelling transitions from the valence into the conduction band become possible close to this atom. After the decay of the core hole, those electrons will partly stay in the conduction band. To conserve the total energy, the energy of the emitted photon is lowered by the energy of the excitation in the sample. This energy loss resembles a shake-up process. This assumption is further supported by the fact that we observe a six times larger emission signal above the fitted band edge as compared to other temperatures. This sudden increase cannot be explained by pure thermal excitation, but is a remainder of the emission spectrum without the creation of electrons in the conduction band. A similar effect is found when analysing the electron–electron scattering contributions at core excited silicon [31].

5. Conclusion

In conclusion, we tracked the thermal evolution of the occupied and unoccupied DOS while directly measuring the asymmetric band gap closing, using temperature-dependent XES and XAS measurements on silicon up to the melting point. We discuss the influence of phonons on the static electronic structure as well as on the measurement process itself, where the former is the main reason for the shrinking of the gap with temperature. A further analysis of our data yields quantitative information about the underlying core-excited state and the connected relaxation energy.

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