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Electron and Hole Dynamics in Silicon-Germanium Alloy Measured by Attosecond XUV Transient Absorption

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Abstract: Electron-hole dynamics is measured by attosecond transient absorption in silicon-germanium alloy. The germanium atoms act as reporter atoms by time-dependent probing the $M_{4,5}$-edge, revealing electron and hole dynamics, as well as a new midgap feature.

The study of carrier dynamics in semiconductors has been an active research field for decades. A profound understanding of the decay mechanism is key for the development of improved semiconductor devices that make up the modern world. Most methods rely on time-dependent changes in transmission and reflection properties in the optical spectral range and can give access to electron dynamics in an excited semiconductor. Likewise, one can access hole dynamics through Raman spectroscopy [1]. However, previously used optical methods lack the ability to observe both species simultaneously and in addition the time resolution is often limited to time scales in the multiple femtosecond range. Remarkable progress towards higher time resolution has recently been achieved using attosecond transient absorption experiments in silicon dioxide [2] and silicon [3]. The silicon $L_{2,3}$-edge at around 100 eV was measured time-dependently revealing subfemtosecond electron dynamics in the conduction band following ultrafast optical excitation. The valence band dynamics, i.e. hole dynamics, were not observed because the silicon $L_{2,3}$-edge requires an excitation from a core *2p* level. As such it has poor oscillator strength to the valence band, which is of *3p* character. Since the electronic properties of a semiconductor are a function of the holes *and* electrons in the valence and conduction band, respectively, it is appealing to find a method for probing both simultaneously. Here attosecond transient absorption experiments performed on excited silicon-germanium alloy are reported. Herein, the Ge atoms are used as reporter atoms [4] for probing the carrier dynamics in the alloy. By time- and energy-resolved investigation of the $M_{4,5}$-edge of the germanium in the alloy, which arises from a *3d* core transition, access to both the valence band and conduction band is achieved at the same time.

A silicon-germanium alloy can be any molar ratio of silicon and germanium $Si_{1-x}Ge_x$, where x is the molar mass fraction. The strained alloy has gained interest in semiconductor industry as it provides the fast response of strained semiconductor layers and thus usability for higher frequency switching with the direct bandgap properties from germanium. This makes silicon-germanium an interesting candidate for CMOS applications that currently rely on GaAs [5]. Another major advantage for industrial applications is that it can be processed using the standard silicon machines. The ability to tune the band gap in the alloy further increases interest in silicon-germanium alloys.

For the experiment, 100 nm thin films of silicon-germanium with a molar mass fraction of 0.5 were deposited using chemical vapor deposition. $Si_{0.5}Ge_{0.5}$ exhibits an indirect bandgap of ~0.9 eV for the given molar mass fraction [6]. For the pump-probe experiment, 5 fs pulses with a central energy of 1.55 eV (Fig. 1a) are divided into two equal paths. The majority of the pulse is focused into a gas cell filled with xenon gas, where high harmonic generation (HHG) up-converts this pulse into the extreme ultraviolet. By employing appropriate gating optics in the arm generating high harmonics, the XUV spectrum is tailored to a continuum spanning 25 to 45 eV (Fig. 1b) suggesting the attosecond nature of the probe pulse. The XUV continuum is ideal for studying the germanium $M_{4,5}$-edge, which corresponds to excitation from the $3d_{3/2}$ and $3d_{5/2}$ core electronic state into the conduction band; the filled valence band is not observed in the unexcited material, but the transition is allowed. The remainder of the pulse is time delayed relative to the XUV pulse, and it is used to pump electrons from the valence to the conduction band in the silicon-germanium alloy (Fig. 1c). After the electrons have been excited to the conduction band, new transitions open up from the Ge 3d to the valence band, allowing hole dynamics to also be observed.
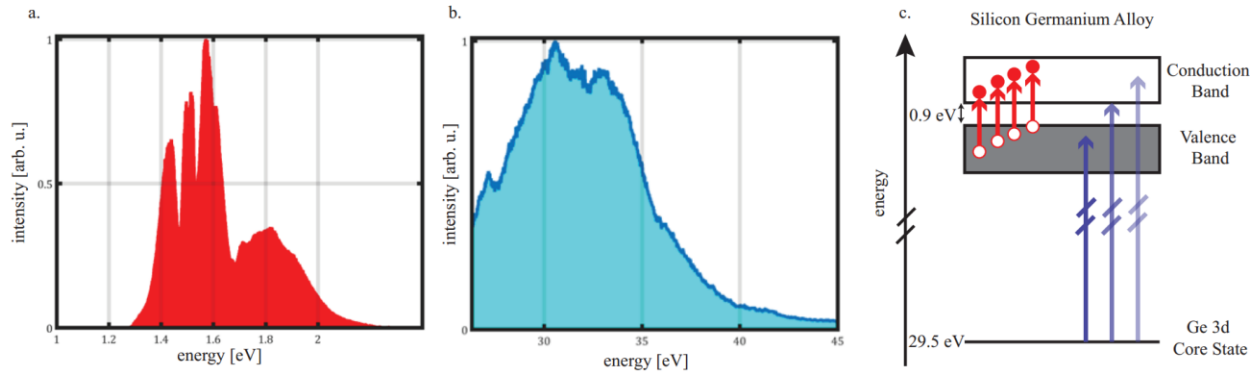
Figure 1a. A spectrum of the 1.55 eV, 5 fs pump pulse used in the experiment and **b.** the XUV probe pulse spectrum used in this experiment. By the nature of the HHG process, it is necessarily temporally shorter than the 5 fs driving pulse. **c.** These two pulses make up the pump-probe scheme. The 5 fs pulse (red arrows) is used to excite electrons (red circles) to the conduction band leaving holes (white circles) behind in the valence band, both of which are probed time-resolved using the XUV pulse (blue arrows) for the 3d core level that exhibits a spin-orbit splitting of 0.57eV.

Since the differential absorption probes from the 3d core level, which exhibits a 0.57 eV spin-orbit splitting for the $3d_{3/2}$ and $3d_{5/2}$ states, one expects to observe the same features shifted in energy and overlapping. Hence it is beneficial to calculate the XUV differential absorption trace for a single spin-orbit state. The summation of the same signal shifted and factorized by the degeneracy of the states leads to a phase term in Fourier space which is known due to known spin-orbit splitting and degeneracies of the states. Hence, dividing the phase factor in Fourier space and subsequent back transformation retrieves the differential absorption related to a single spin-orbit state.

The measured and spin-orbit corrected differential absorption, also called differential optical density (ΔOD), as a function of time delay is shown in Figure 2. Positive time delay refers to a scheme where the NIR-VIS pump pulse arrives first and the broadband XUV pulse subsequently probes the absorption. Two major features are apparent at times after the ultrafast excitation. At photon energies 30-31.2 eV negative differential absorption, i.e. increased transmission, is evident which is related to electrons that are promoted to the conduction band (CB). Likewise, at photon energies 28.5-29 eV an increase in differential absorption suggests an increase in hole density in the valence band (VB). The energy gap between these two features of about 0.95 eV (dotted lines in Fig. 2) compares well to the expected band gap of $Si_{0.5}Ge_{0.5}$. A comparison to measurements in pure germanium which are supported by time-dependent density functional theory (TD-DFT), not shown here, gives confidence that indeed energy-resolved dynamics of holes and electrons in the valence and conduction band (CB) respectively can observed at the same time.

Detailed analysis of the rise of the observed signals show that the population change follows the excitation pulse closely and is instantaneous within the instrument response time limited by the pulse duration of the pump pulse (about 5 fs). The VB shows a slow dynamic red-shifting after excitation and relaxation back to the upper edge of the VB within 300 fs followed by slow decay in a time scale beyond a picosecond. This can be understood by holes scattering towards the upper valence band edge. The negative signal around 30.3 eV, related to electrons in the conduction band, shows decay towards lower energies that can be understood as scattering into energetically deeper lying regions of the conduction band and subsequent decay, both by scattering of phonons heating up the lattice. The slight positive feature towards higher time delays in the conduction band is likely related to a heating of the lattice, which causes a renormalization of the band structure leading to a positive feature covering the electron signal. Hence, it is assumed that the electrons decay on time scales comparable to the holes, however, phonon-related renormalization creates an increasing positive feature in the same energy range covering the electron signal. More interestingly, a feature is observed in the midgap at around 29.8 eV. This feature is established upon excitation and decays within about 200 fs. The feature is localized in energy and does not exhibit time scales similar to the other features, hence it appears to be a separate feature. A possible explanation is that dangling bonds, that have an elevated density in the investigated alloy and typically generated midgap states [7], are photoexcited by the laser alongside the electrons promoted from the valence to the conduction band. Due to energetic proximity to the conduction these unpaired bonds can fill up fast by electrons relaxing in the conduction band due the conduction band tail reaching energetically into the region of the midgap states.
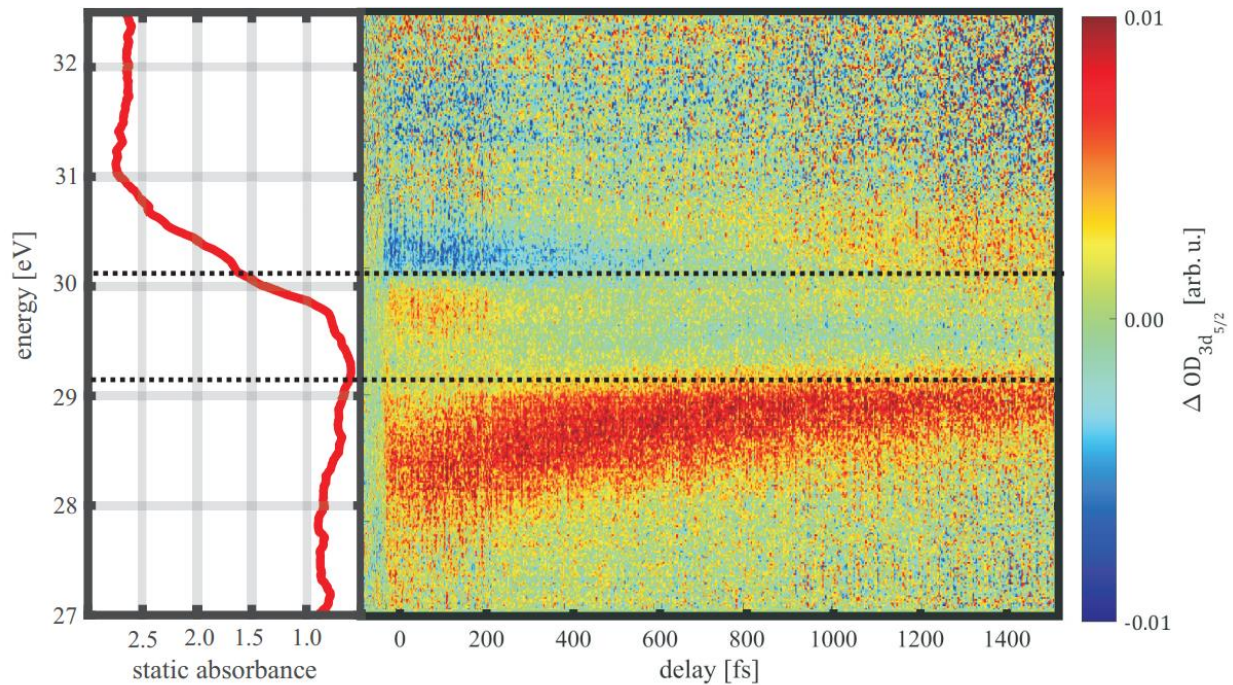
Figure 2. (Left) Measured ground state absorption spectrum of the $M_{4,5}$-edge related to germanium in the silicon-germanium alloy. (Right) Differential absorption at different time delays (color bar on the right) for the $3d_{5/2}$ state, i.e. contributions by the $3d_{3/2}$ state are removed. Negative time delays correspond to the XUV pulse arriving first and positive time delays correspond to the 5 fs pump pulse arriving first. The Fermi level is at about 29.6 eV. The lower and upper edges of the conduction and valence band, respectively, are indicated by the dotted lines.

Current investigations aim at a better understanding of the dynamics observed in the energy- and time-resolved differential absorption spectrum in order to relate the observed features to properties of the material. By comparing the results from the alloy to pure germanium samples that were measured in the same experimental run and are supported by TD-DFT calculations, a principal understanding of the alloy can be achieved. Ultimately, a future goal is to implement a full TD-DFT simulation directly for the alloy.

In this work attosecond transient absorption measurements in silicon-germanium alloy that allow for simultaneous probing the electron and hole dynamics are presented. Signatures of other quasi particles such as phonons can be identified by renormalization effects. In the presented experiments the germanium atoms are employed as reporter atoms for the alloy. This method allows not only direct access to the dynamics of both carrier species that are relevant for the electronic properties of a semiconductor, but also provide for a superb energy resolution (about 100 meV in the presented data) of the dynamics along with ultrafast temporal resolution. A midgap feature suggests excitation of dangling bonds in the amorphous silicon-germanium alloy and subsequent neutralization of the bonds on a sub-200fs time scale. Further investigations on this material are justified because dangling bonds are understood as source of losses in solar material based on such semiconductors.

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