PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN 49 (1980) SUPPL. A p. 133–136

PHOTOEMISSION FROM ELECTRONICALLY EXCITED SEMICONDUCTORS

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We have studied the electronic structure of semiconductors which are in an electronically excited state created by a strong laser pulse. The valence band photoemission of the excited sample exhibits drastic changes compared to the ground states. In the Si 2p core level spectrum appears a satellite peak which is not present in the unexcited sample. These observations lead to the conclusion that a core exciton of about 2eV binding energy exists in the excited sample.

Using angle resolved photoemission in coincidence with a pulsed, frequency doubled Nd:Yag laser beam ($\hbar\nu_L$ = 2.33 eV), we have studied the dynamic rearrangement of the electronic states in Si in the presence of a large number of electron hole pairs created by laser photon excitation. We observe drastic changes in the valence bands, a renormalization of the bandgap, and a satellite peak in the Si 2p core level photoemission. Photoconductivity measurements indicate a very long recombination time for electrons in the conduction band of about 20 μsec at room temperature [1]. This allows us to study the dynamic response of the electronic states to these excitations by measuring the angle resolved photoemission of the valence band in coincidence with a laser pulse. Upon excitation of an electron from the valence band into the conduction band, its wavefunction and charge density change. This causes, if the density of excited electrons is high enough, a self consistent rearrangement of all electronic states. We want to demonstrate these effects here for the case of Si.

The samples were Si(111) single crystals cleaned in situ by heating to remove the oxygen contamination and a light sputtering and annealing to remove carbon built up on the surface. We used a Chromatix 1000 E frequency doubled Nd:Yag laser with a pulse rate of 600 Hz and $1.6*10^{15}$ photons per pulse. Thus, we achieve a density of $1.2*10^{21}$ electron hole pairs per cm^3 in the excited state of the sample. The spectra were taken in coincidence with the laser pulses, using an angle resolving photoelectron spectrometer [2] which is coupled to a toroidal grating monochromator at the Tantalus I storage ring of the Synchrotron Radiation Center of the University of Wisconsin-Madison.

Fig. (1) shows the valence band photoemission of Si in the ground state and in the presence of the laser excited electron hole pairs. The ground state curve can be well understood in terms of the density of states of the valence band [3]. Due to the 7 x 7 reconstruction of the surface, no large angular effects are expected in the spectra. The difference curve at the bottom shows not only the depletion of the valence band close to the top (neg. peak at -0.7 eV), but changes down to -10.9 eV where a new peak appears. These changes in the valence band structure are a direct consequence of the charge rearrangement

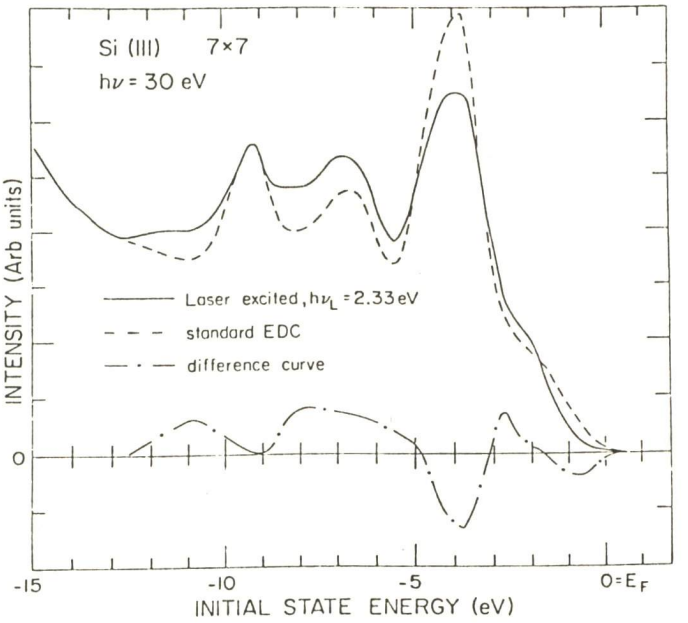

Fig. 1 Angle resolved photoemission curves of Si(111) excited by a frequency doubled Nd:Yag laser beam in comparison with the emission of the same crystal in the ground state: The difference curve is shown at the bottom

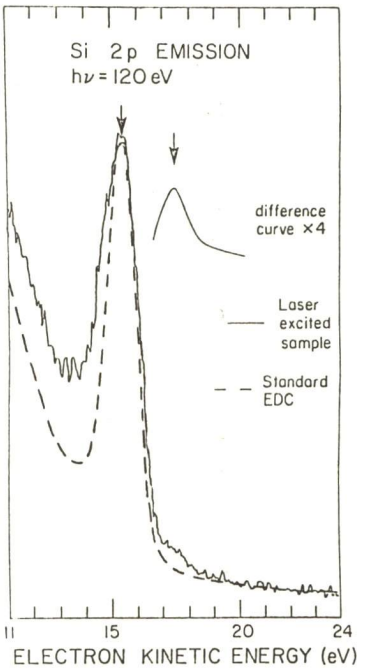

Fig. 2 Si 2p photoemission showing a satellite peak and broadening in the excited state: The spectrum of the excited sample is a reproducing of the original chart recorder trace

between the top of the valence and the bottom of the conduction band. The broadening of the features can be understood by an increased electron phonon scattering. Following the initial electronic excitation, the excited electrons scatter into the minima of the conduction band creating a large number of phonons. Nevertheless, the lattice temperature rise has been measured to be 300°C at a laser power of 1 J/cm^2 [4], and should be much smaller in our case. All the observed changes are reversible and not due to a reconstruction.

The Si 2p core level photoemission shows a satellite line shifted by 2.0 ± 0.3 eV to higher kinetic energy (Fig. 2). The shifted peak originates from an atom in the vicinity of which there was an excited conduction electron that screens the core hole potential more effectively and therefore lowers the apparent binding energy of the 2p photoelectron. The area ratio of both peaks (36:1) agrees with what we expect from the estimate of the number of excited states. The main line is slightly broadened and the background increases in the excited state; both effects might again be due to an increased electron phonon scattering.

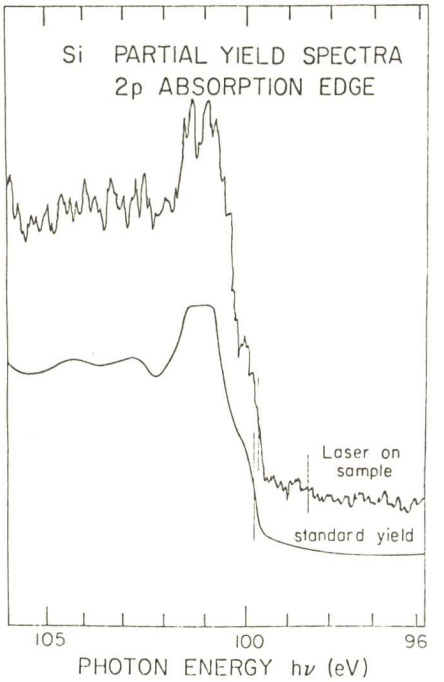

Fig. 3. Partial photoyield of Si at the onset of the 2p to conduction band transitions: The spectrum taken in coincidence with the laser photons is shown in the original form

In Fig. (3), we show the partial photoyield of the sample around the onset of the 2p transitions, which is equivalent to the bulk absorption in this energy range. For the excited sample, we observe a slight shift of the 2p absorption edge by 70 ± 30 meV to lower energies in accordance with calculations by Brinkman and Rice [5]. The weak structure at the onset of the edge is caused by transitions into the lowest excited state of the core hole equivalent to the satellite peak in the 2p photoemission.

The magnitude of the 2 eV shift of the core photoemission line, as well as the position of the structure at the onset of the adsorption, is not easily understood. Both indicate that it is possible in the case of the laser excited sample to create a 2p core hole with an energy of 2 eV less than for normal Si. Both features are explained if core exciton exists that has a binding energy of approximately 2 eV. For Si in its ground state, there are, however, no indications for such an exciton. If a core exciton exists at all, it has a much

smaller binding energy. Moreover, it has been observed that valence band excitons in GaAs cease to exist under laser irradiation [6]. Valence band excitons have according to their binding energy a radius of about 20 Å. Therefore, in the laser excited sample, the hole potential gets screened by the electrons in the conduction band and no exciton absorption line is obscured anymore. The radius for an exciton having a binding energy of 2 eV is much smaller. It still might be able to exist in a sample with a high density of conduction electrons. Moreover, since it is not observed for Si in the ground state, the existence of this excitonic state and its binding energy might depend on the density of conduction band electrons in the sample. Further support for this conclusion is gained from the presence of structures observed in electron energy loss measurements located about 2 eV below the 2p to conduction band transitions [7]. In this case, the conduction band is flooded by the electrons of the beam used to scatter from the sample and the generated secondary electrons quite analogous to our experiments.

This work was supported by the NSF-MRL program under Grant No. DMR 76-80994. The Synchrotron Radiation Center was supported by NSF Grant No. 77-21888.

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