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TWO QUANTUM PHOTOEMISSION IN SEMICONDUCTORS

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Abstract

Two-quantum photoemission is a process in which two times the photon energy is transferred to the photoelectron. In this process, the photoelectron observed in the vacuum keeps a "memory" of the intermediate empty state by which it transited after its first excitation, and before its second excitation and its final escape. We discuss here the experimental problems involved and the information obtained in the case of the semiconductors Si and InP. We show that ballistic or non-ballistic electrons can be selected by an adequate choice of experimental conditions, yielding information on both the static and dynamic properties of the empty states.

Key words: photoemission, multiphoton excitation, surface, empty states, ballistic electrons, relaxation processes

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Introduction

According to the first photoemission experiments, no electron could be emitted by a solid under irradiation, no matter how intense, unless its wavelength was lying under a value which was characteristic of the solid. This "photoelectric effect", which is one of the first demonstrations of the quantum nature of light, is now interpreted in terms of a threshold photon energy. The difference between the Fermi level -highest occupied level- and the vacuum level -lowest energy level at which an electron can leave the solid- is the work function. If the photon energy is smaller than this value, no optical transition can bring the electron above the vacuum level and no photoemission is observed, whatever the photon flux. Actually, this last sentence stands true only as long as this flux remains "weak". Under "strong" illumination, photoemission can occur at photon energies lying below the work function, because the light beam can transfer more than one quantum of energy to the electron by non-linear processes. These processes which will be described further on have very low quantum yields and their observation requires very high light intensities: "strong" illumination means here perilously close to the optical damage threshold. However, non-linear photoemission has been observed on a variety of materials, including metals, alkali halides, organic compounds (see a reference list in Bensoussan and Moison, 1982). Work on semiconductors includes Te (Wautelet and Laude, 1977), Ge (Laude et al. 1977), PbI_2 and GaS (Kasuya et al. 1978), Si (Eberhardt et al. 1982, Malvezzi et al. 1984), GeSe (Kasuya and Nishina 1981), ZnTe and CdTe (Williams et al. 1981 and 1982), and InP (Haight et al. 1985). We discuss here the experimental problems involved and the information that non-linear photoemission - and mainly two-quantum photoemission (2QP) - can bring out, with reference to our published studies of silicon and to new data on indium phosphide.

The observation of two-quantum photoemission

In a linear or one-quantum photoemission

(1QP) process, the photoelectron flux is proportional to the photon flux. Their ratio which is known as the 1QP quantum yield lies around 10^{-3}. In a two-quantum process, the photoelectron flux is proportional to the square of the photon flux, with a proportionality factor, or "two-quantum yield", lying in the 10^{-30} $cm^2 x$ s range. Therefore, under a common $1mW/cm^2$ excitation, the yield of two-quantum photoemission is 10^{+12} times smaller than the one of one-quantum photoemission. They would become equal only at $1MW/cm^2$. It follows that 2QP can be observed clearly only 1) at photon energies below the work function, where one-quantum photoemission vanishes, and 2) at light intensities where continuous-wave irradiation would induce optical damage. However, with an excitation provided by nanosecond visible-UV lasers, and solid-state photocurrent detectors, 2QP can be observed over a range extending down to a thousandth of the damage threshold ($10kW/cm^2$) (Bensoussan et al., 1981).

At the high intensities involved, many phenomena can take place besides 2QP, and a primary concern in such experiments is to avoid those which can bias the 2QP measurements. For instance, in the case of silicon, the occurrence of surface modifications (Moison and Bensoussan, 1983a), electron thermoemission (Bensoussan and Moison, 1981), three-quantum photoemission (Bensoussan and Moison, 1983a), surface heating (Lietola and Gibbons, 1982), non-linear optical absorption (Moison et al.,1983), photovoltage, etc..., and of course 1QP limit the observation range severely (see figure 1).

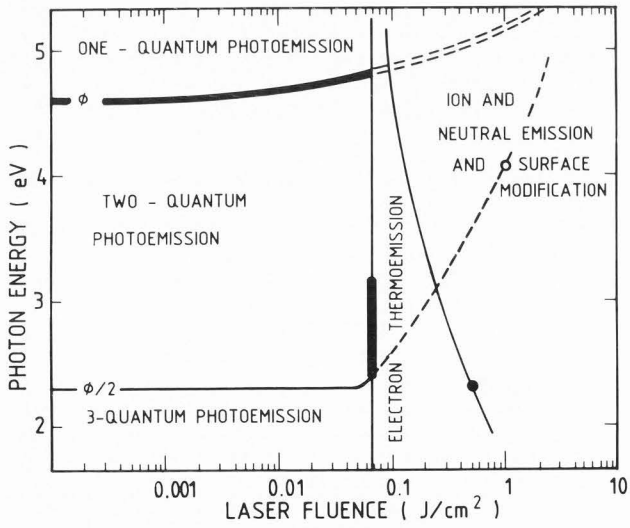

Figure 1 : Various processes observed on Si(111) under nanosecond excitation as a function of laser fluence and photon energy. Heavy lines and dots represent actual measurements. Light lines are extrapolations. Dotted lines are virtual borders. ϕ is the work function.

However, in this range, we check the quadratic flux law over six orders of magnitude of photoelectron flux (figure 2), by varying the beam energy and impact area, which are under constant and careful monitoring (Bensoussan et al.,1981). This measurement gives an accurate value of two-quantum yield, as a function of the photon energy (Moison and Bensoussan, 1981). We also determine the energy distribution of the photoelectrons with an energy analyzer whose resolution is 100meV (Bensoussan and Moison, 1983a, b).

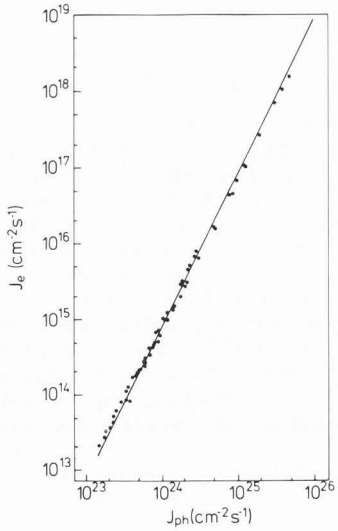

Figure 2 : Log-log plot of the photoelectron flux Je vs photon flux J_{ph} at a photon energy of 3.68eV on Si(111). The slope of the solid line is 2. The 2QP yield deduced is (1.05 ± 0.15) x 10^{-34} cm^2 x s.

Finally, 2QP like most processes involving low-energy electrons is very sensitive to the state of the sample surface. Therefore, its surface must be prepared under ultra-high-vacuum conditions and monitored by techniques like low-energy electron diffraction, Auger electron spectroscopy, or X-ray photoelectron spectroscopy. Furthermore, the photoelectron energies measured are referenced to the vacuum level. In order to position them in the bulk and surface band structure of the material, the work function, the ionization energy (vacuum level - valence band maximum VBM), and the density of surface states - if any - which depend on the surface configuration must be determined in-situ by ultra-violet photoemission spectroscopy and Kelvin probe.

The three-step model

As a first step in the interpretation of 2QP data, it may be observed that 2QP at a photon energy E and 1QP at a photon energy 2E transfer the same energy 2E to the electrons. The final states in the vacuum and hence the initial states involved in both processes are identical. For this reason, we can describe 2QP by the classical "three-step model" (Berglund and Spicer, 1964) whose success in the field of 1QP is remarkable. This model divides the overall photoemission process into three successive steps : 1) photo-excitation of the electron from its initial state to its final state in the crystal, 2) transport to the surface, 3) escape into the vacuum (figure 3).

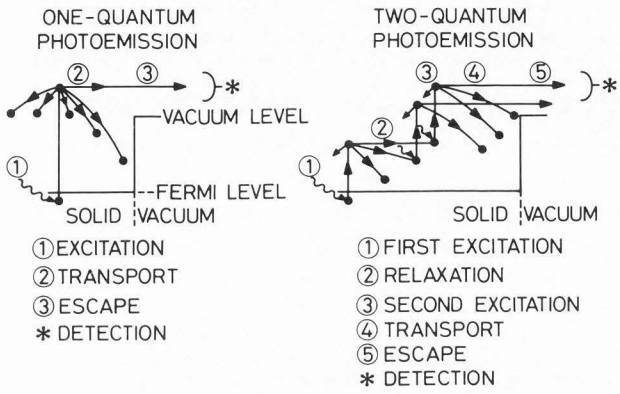

Figure 3 : Multistep models of one-photon and two-photon photoemission

Very little is known on the two final processes, but they are identical for 1QP and 2QP as the final states are identical. The transport is usually taken into account by an escape depth L : an electron at a depth z has a probability exp(-z/L) of reaching the surface without being scattered. Such electrons are known as primary or ballistic electrons. As the escape depth lies around 10 Å for low-energy electrons (5-10eV above the Fermi level), photoemission is very surface-sensitive, and nearly instantaneous, because the escape time is very short (10^{-14}s). The escape step is described by an escape probability function, taken equal to zero when the final state lies under the vacuum level, and to one otherwise. Actually, these two last steps are rather neutral, and the photoemission data roughly reflects the excitation step, which in turn depends on the band structure and on the excitation process.

Two-quantum excitation processes

In the case of 2QP, the excitation process is not a mere optical transition as in the case of 1QP, because it involves the transfer of two energy quanta. This is clearly demonstrated by three observations : 1) the relation between photon flux and photoelectron flux is quadratic (figure 2), 2) no 2QP can be observed for photon energies below half the work function (figure 4), and 3) the upper level at which an electron can be brought is exactly the Fermi level plus twice the photon energy (figures 5 and 6).

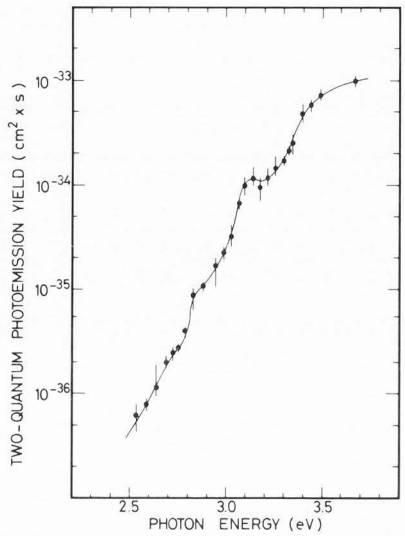

Figure 4 : Two-quantum photoemission yield vs photon energy on Si(111)

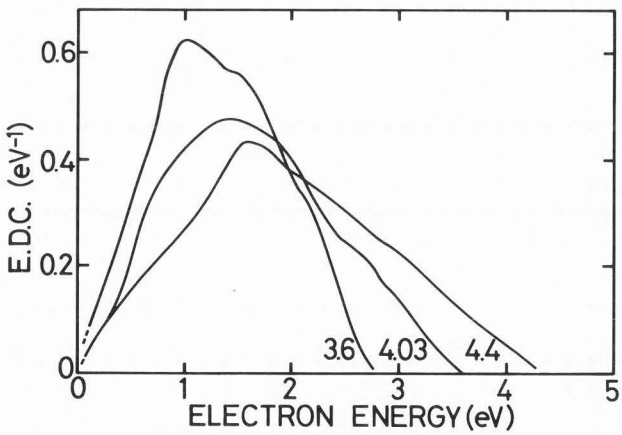

Figure 5: Normalized energy distribution curves (E.D.C.) vs photoelectron kinetic energy, at three different photon energies, on Si(111)

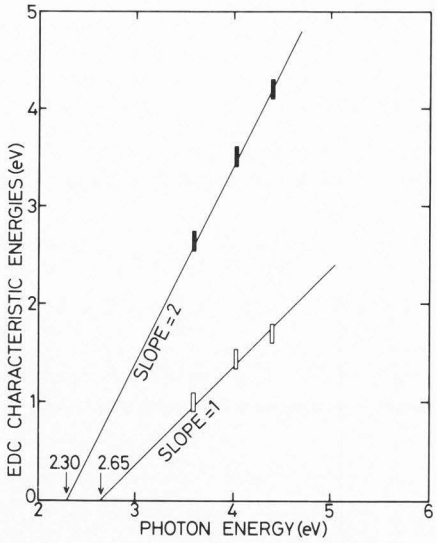

Figure 6 : Characteristic energies of the energy distribution curves on Si(111) (figure 5) vs photon energy : high-energy end (full symbols) and peak position (open symbols). 2.30eV is half the work function. 2.65eV is the position under the vacuum level (2.70 eV above the valence band edge) of the critical point in the intermediate level.

Several processes which transfer two quanta can be put forward. Some of them involve a simultaneous transfer like second-harmonic generation followed by optical absorption, or two-photon absorption via a virtual intermediate state. Others involve successive transfers of a single quantum via a real intermediate state, like optical absorption followed by either free-carrier absorption or non-radiative Auger process. If the first ones are operative, no influence of the intermediate state is expected, except possibly for the selection rules, and 2QP at a photon energy E and 1QP at energy 2xE are similar processes. However, the experiments show that both the related yield spectra and energy distributions are clearly different. The excitation process does involve a first excitation, a stay at the intermediate level and a final excitation. Actually, the energy distributions show that 2QP is mainly governed by the intermediate state, as their main peak moves like the photon energy (figure 6) and therefore originates from a constant intermediate level.

Two-quantum photoemission and the study of empty states

This sensitivity to the intermediate level is a prime feature of 2QP, because it gives access to information about the normally unoccupied states located above the Fermi level. Such information, which is very important for both theoretical and applied purposes, is by now obtained from calculations, from rather indirect transport measurements, or more recently from inverse photoemission (low-energy cathodoluminescence). The 2QP approach of this problem is to populate first the empty levels with electrons, and to take them out into the vacuum before they are recombined. In this respect, 2QP can be described by a five-step model including 1) optical excitation from the initial level to the intermediate level, 2) scattering, drift diffusion and recombination in the intermediate level, 3) excitation to the final level, 4) transport to the surface, 5) escape (figure 3). Obviously, the transit time of the electron in the intermediate level is of prime importance in the information gained. If this transit time is short with respect to the intra-band relaxation times, the final states reflect the distribution of intermediate states as created by the first excitation and information on the band structure can be obtained through adequate selection rules. If, on the contrary, the transit time is long, the final states reflect the distribution of relaxed intermediate states. This shows that 2QP can potentially give information on both the static and dynamic properties of empty states. It may be emphasized that it also yields absolute values for the levels involved, while purely optical experiments yield only transition energies, and that it is basically surface-sensitive, and can therefore deal with surface empty states as well.

Ballistic and non-ballistic electrons

In principle, the two kinds of electrons in the intermediate states, primary and secondary, or ballistic and non-ballistic, should be observed simultaneously by 2QP. However, photoemission possesses a built-in energy high-pass filter, the vacuum barrier. An electron in the intermediate state, which had just enough energy to leave the solid after the second excitation, and which undergoes a slight energy relaxation, cannot contribute any more to photoemission. Therefore, the contribution of ballistic electrons is outstanding at low photon energies. On the contrary, at high photon energies, both ballistic and relaxed electrons can be extracted from their intermediate levels. As it is expected that electrons that have relaxed down to critical points of the band structure have a longer transit time in these particular intermediate levels, the corresponding 2QP yield should be greater than the one corresponding to ballistic electrons the contribution of electrons relaxed in long-lifetime levels is outstanding at high photon energies.

The first regime is clearly exemplified by the case of silicon (111). The energy distributions observed can be correctly described by a product of initial, intermediate and final density of states separated by the photon energy, i.e.,by assuming that no energy relaxation takes place in the intermediate level

(Bensoussan and Moison, 1983a, and Moison and Bensoussan, 1983b). The features in the yield spectrum can be associated with singularities of optical transitions. Surface-related initial states can be detected (Bensoussan et al., 1980).

Similar observations are made on InP(100) below 3.6eV. On the contrary, above this photon energy, a new regime is observed : the yield increases very rapidly (figure 7), and the energy distribution turns to a sharp peak moving with photon energy (figure 8). In this regime, the intermediate level from which electrons are extracted by the second excitation is accurately located and does not depend on the energy of the first optical excitation. This is confirmed by two-beam (pump/probe) experiments. Considering the location of the critical level at 2.2eV above the valence band maximum, it can be associated with a lateral (X or L) valley or with a surface state. The electron lifetime in this level is much longer than in those involved in the first regime. However, by introducing defects at the surface and therefore decreasing this lifetime, we observe a quenching of this "non-ballistic" regime and a return to the "ballistic" regime.

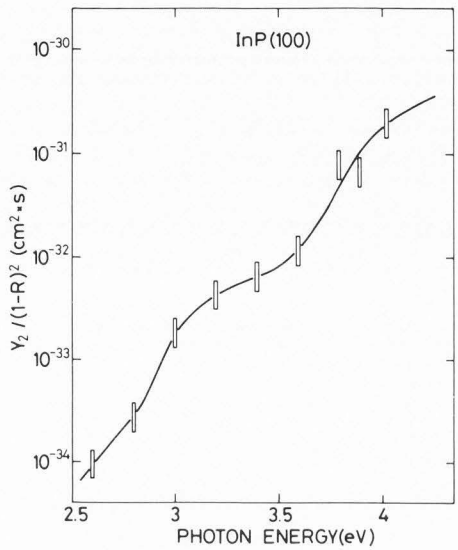

Figure 7 : Two-quantum photoemission yield vs photon energy on InP(100)

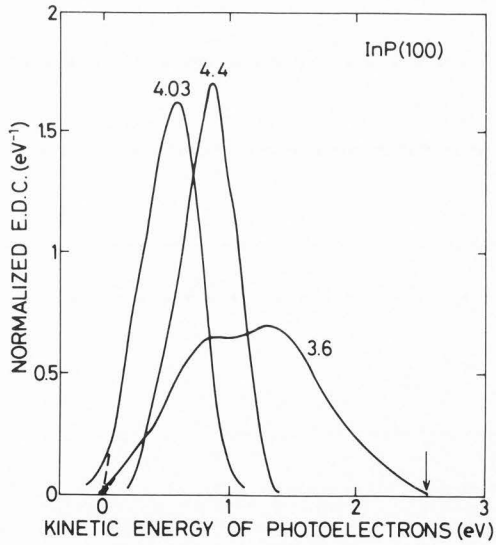

Figure 8 : Normalized energy distribution vs photoelectron kinetic energy, at three different photon energies, on InP(100).

The future of two-quantum photoemission

The need for information about the empty states of semiconductors and about the dynamics of injected carriers is increasing, for instance in microelectronics with the development of high-speed "ballistic" devices. In this field, the 2QP approach which is now proven to be realistic may prove fruitful. With two-beam experiments, electrons can be injected at given energy levels, and then probed with time and energy resolution along their relaxation path : 2QP may be described as a contact-less, energy-resolved, transport technique. It is hoped that 2QP can bridge the gap between experiments where very short times are involved, like inverse photoemission, and transport experiments which deal with longer times.

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Discussion with Reviewers

L.L. Levenson : The very high sensitivity for the two-quantum photoemission process to surface contamination appears to have certain benefits as well as limitations. If the power input to the surface is too small, the 2QP process will be too small to observe. If the power input is too high, there will be competition between surface segregation of impurities and desorption of impurities. How well can you characterize the state of the surface in the area of the photon beam impact as a function of the number of pulses ?

Authors : The question addressed, whether the high powers needed to observe 2QP modify the surface under investigation or not, is for certain very important. In the case of Si, InP or GaAs, and under visible-UV nanosecond irradiation, where only $10^{-4}J/cm^2$ is needed we are fairly confident that such surface "damage" as evoked in the question can be avoided, for two reasons : 1) all calculations (see Lietola and Gibbons, 1982) and our own unpublished data on simultaneous photoluminescence show that the beam-induced temperature increase is negligible at such fluences ; 2) our measurements of the surface structure after irradiation (Moison and Bensoussan, 1983a) by surface-sensitive techniques demonstrate that no surface damage is observed below $0.1J/cm^2$, i.e. a thousand times the fluence required to observe 2QP. Finally, we would like to point out that electronic perturbations, like band filling, are much more difficult to avoid than surface damage, and of course that different conclusions would probably be reached for other irradiation conditions and other materials.