Electron-energy distribution in silicon under pulsed-laser excitation

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By yield and energy-distribution measurements, we identify two photoemission regimes from silicon under nanosecond laser irradiation. At low fluence and high photon energy, two- and three-quantum processes are the main emission mechanisms; effects of initial and intermediate states are the dominant spectral features. At high fluence and low photon energy, thermoemission prevails and is characterized by a Maxwellian distribution with a temperature different from that of the lattice during the excitation pulse.

Optical excitation is by now the most widely spread spectroscopic method used to probe the electronic structure of solids. With photon energies larger than the work function Φ, photoemission is considered to be the most powerful technique,[1] while with photon energies smaller than Φ optical experiments and luminescence studies are still the best way to get information on electronic transitions and hot-carrier processes.[2] In the energy range between vacuum level and Fermi level, nonlinear photoemission (NLP) gathers the capabilities of both photoemission and nonlinear optics, as it may yield absolute energy locations and additional selection rules. Unfortunately, the quantum yield of the processes involved is usually very low and strong illumination by powerful pulsed lasers is required. At such levels, spurious effects such as surface change, ion emission, melting, etc., can occur simultaneously and make the observation of NLP difficult. On the other hand, for this very reason, this technique is particularly well suited for studying the underlying physical mechanisms in the new laser processing technology which are still under discussion, despite a great deal of experimental and theoretical activity.[3]

In previous papers, we have demonstrated both of these capabilities in the case of silicon. We have shown[4] that, under nanosecond laser excitation with photon energies smaller than Φ, electron photoemission takes place at fluences more than two orders of magnitude smaller than the usual processing levels. In this regime, the photoelectron flux is proportional to the square of the photon flux, and this behavior, as well as its dependence on photon energy,[5] is typical of a two-quantum photoemission (2QP) process. The comparison with linear photoemission experiments reveals the influence on the 2QP of the intermediate state involved. On the other hand, at high fluences and low photon energies ($< \Phi/2$), the photoelectron flux increases very rapidly with the photon flux, and this regime is correctly described by a thermoemission (TE) process from a hot electron gas, thus yielding the electron temperature.[6] These yield measurements show that NLP provides a direct probing of both the primary and secondary electron population created by intense photoexcitation. This performance can be improved by the determination of the energy spectrum of the photoemitted electrons. In this Communication, we report such measurements on silicon, under various laser illumination conditions. Our results confirm the existence of the two regimes, i.e., 2QP and TE. Moreover, we show by a partial-yield technique that, at high photon energies and high fluences, three-quantum photoemission occurs. Beyond the identification of the emission processes, the energy analysis shows that the linear photoemission approach can be successfully extended to NLP, and reveals new information on the energy levels involved.

The experimental technique we used to determine the energy-integrated yield Y and its spectrum $Y(E)$ has been described elsewhere.[4] The sample is a (111) n-doped silicon wafer cleaned and annealed under UHV conditions to obtain the equilibrium (7×7) surface structure, as checked by *in situ* surface techniques. An excimer-laser-pumped dye laser beam, whose characteristic features (pulse duration ~ 5 ns, energy/pulse, and energy distribution) are carefully monitored, is focused on the sample. Photoemitted electrons are collected by a spherical collector brought to an attractive voltage and connected to a charge amplifier. For energy analysis purposes, an extra set of four grids is used in the classical retarding-field configuration to obtain high-pass energy filtering. This configuration minimizes the space-charge effects critical in pulsed experiments, and a saturation plateau is observed at zero contact potential difference. The energy distribution curve (EDC) is obtained by numerical derivation. The overall resolution is about 200–300 meV, as deduced from experiments on copper samples.

Figure 1 shows the EDC's (dY/dE normalized to unity area versus electron kinetic energy) at different

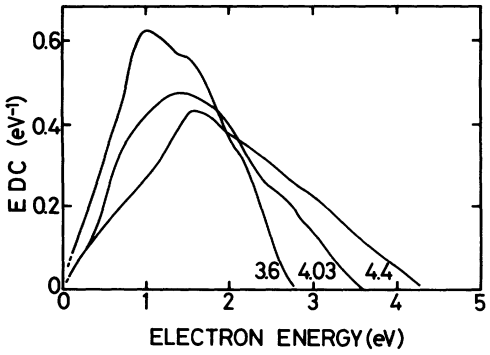

FIG. 1. Normalized energy distribution vs electron kinetic energy, at three different photon energies: 3.2 eV at 0.035 J/cm^2, 4.03 eV at 0.005 J/cm^2, and 4.4 eV at 0.0006 J/cm^2.

photon energies and low fluences (EDC's do not depend on fluence, up to a level where another process takes place, which will be discussed further on). The energy extension of the EDC's is equal to what can be expected from a 2QP model, i.e., $2E-\Phi$. This is clearly shown by plotting the high-energy end of the EDC vs E (Fig. 2): The kinetic energy of these high-energy electrons increases as $2E$ and the threshold energy is found to be 2.3 eV ($\Phi/2$). On the same figure, the position of the maximum of the EDC's is plotted versus E; this position varies as $E-E_i$, with $E_i=2.65$ eV. By extension of the linear photoemission approach,[7] we deduce from this variation that this broad peak corresponds to a feature of the electrons in the intermediate state involved in 2QP. From the value of E_i, we find that this feature is centered at 2.8 eV above the top of the valence band. The EDC peak is too broad to be ascribed to a single transition at a critical point of high symmetry in k space, but more likely arises from a number of transitions in various parts of the Brillouin zone. The lowest conduction band and the highest valence band are 3.2 to 4.5 eV apart and slope downwards along the (111) and the (100) direction.[8] This shifts the maximum of the EDC to a lower energy and explains the peak at 2.8 eV. This peak is, therefore, due to transitions which occur over a large region in k space, and the shape of the EDC corresponds to the product of the initial, intermediate, and final densities of states.[9]

It must be noted that the contribution to 2QP of secondary electrons is not important. Actually, electron scattering mechanisms, whose characteristic times [10 ps (Ref. 10)] are much smaller than our pulse duration, must build up a huge carrier density at the bottom of the conduction band; in a two-quantum process, the cascade photoexcitation of these electrons could give a large contribution to the low-energy region of the EDC's. This is not what we observe because of the low yield of this process at high photon energy as compared to the primary process[6,9]. This point is confirmed by the variation of the EDC's with laser fluence, which does not show any enhancement of the low-energy contribution, as could result from increasing the carrier density and the scattering efficiency. This variation is shown in Fig. 3 at $E=4.03$ eV, with laser fluences kept below

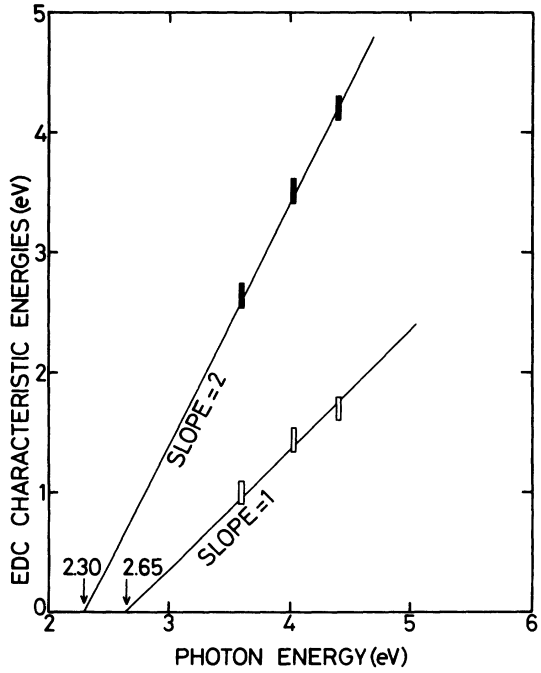

FIG. 2. EDC characteristic energies vs photon energy: high-energy end (full symbol) and peak position (open symbol).

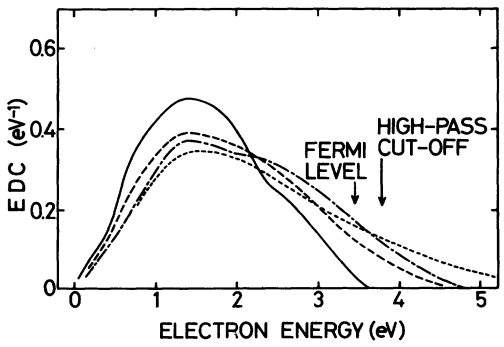

FIG. 3. Normalized EDC's at different laser fluences: ——0.005 J/cm^2; – – –0.016 J/cm^2; ——-0.029 J/cm^2; - - - -0.060 J/cm^2. Photon energy is 4.03 eV.

the damage level. In the fluence range considered, the flux square law is still roughly obeyed, which is typical of a 2QP process. However, the main effect of increasing fluences is clearly the appearance of electrons having kinetic energies much too high to result from 2QP mechanisms. This broadening of the EDC can be attributed neither to a thermal broadening of the photoemission threshold nor to a change of the work function. We have selected these high-energy electrons by a high-pass energy filter located just above the 2QP Fermi edge (see Fig. 3). The partial electron flux deduced from this measurement is found to be proportional to the cube of the photon flux, which is typical of a three-quantum photoemission (3QP) process, and the new width of the EDC is also in agreement with this model ($<3E-\Phi$). The corresponding 3QP yield is 2×10^{-59} cm^{4}s^2; similar values have been reported on other materials.[11] A number of processes can account for this 3QP behavior, among them three-photon absorption, or combinations of Auger biparticle recombination and one-photon absorption. But whatever the mechanism, the major fact is the existence of electrons with energies as high as 10 eV above the bottom of the conduction band. Now the efficiency of such electrons in promoting electrons from the valence band into the conduction band by impact ionization can be very high.[12] Therefore, if thermal effects do not prevail first, optical breakdown of the material is likely to take place by avalanche multiplication of carriers. It must be noted that, at the fluences currently used in laser processing, even if this catastrophic phenomenon does not occur, high-order nonlinear processes do occur and must be taken into account in the overall energy balance.

At lower photon energies, the multiquantum yields decrease significantly and the observation of the thermoemission effect becomes possible. At fluences above 0.01 J/cm^2 for $E<3$ eV and at any fluence for $E<2.3$ eV ($=\Phi/2$), the increase of the photocurrent with fluence becomes highly nonlinear and does not fit any multiquantum model with a definite power law.[6] A similar behavior has been reported on other materials, especially metals.[11] As mentioned before, we have interpreted this effect as a thermoemission from the hot electron gas created during the laser pulse.[6] Under this assumption, if the gas is in internal equilibrium, the EDC of the outgoing electrons must have a Maxwellian shape. Because of the low yield of the process at low fluences, the EDC could be determined only at high fluences (0.7 J/cm^2), near the damage limit (Fig. 4). The experimental data fit fairly well a Maxwellian distribution on the high-energy side of the EDC and an electron temperature of 3700 ±300 K may be deduced. On the low-energy side, a deviation is observed, indicating a deficiency of low-energy electrons. This may be due to a number of factors, such as space-charge effects,

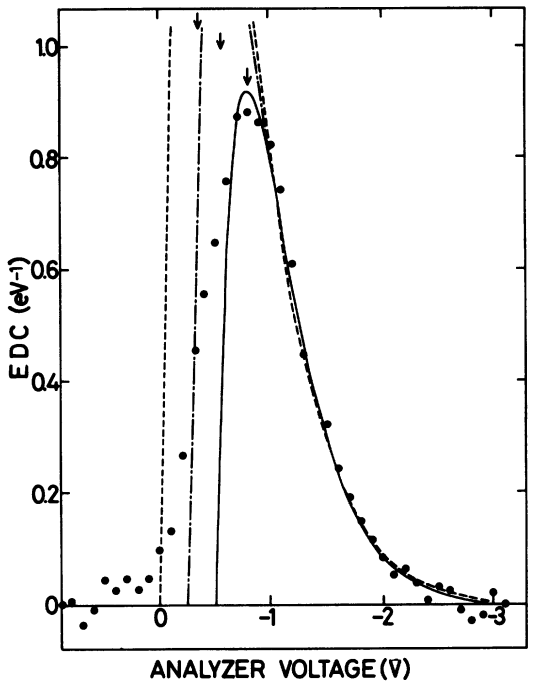

FIG. 4. Normalized energy distribution vs analyzer voltage (full circles); the three curves are Maxwellian fits with various work function changes $\Delta\phi$: $---\Delta\phi=0$; $-\cdot-\cdot-$ $\Delta\phi=0.25$ eV; —— $\Delta\phi=0.5$ eV. The laser fluence is 0.7 J/cm^2 at 2.3 eV.

reflection at the surface, simultaneous emission of ions, or work function change induced by a modification of the surface[13] (see Fig. 4). However, the good overall Maxwellian fit of the EDC which deviates strongly from the EDC observed in the MQP regime confirms our thermoemission model. Here again, the electron temperature obtained is clearly too high to be also the one of the lattice, and we infer that we indeed measure the temperature of an electron gas which is not yet in equilibrium with the lattice. As the electron-lattice relaxation times are very short, this is possible only as a transient state during the excitation pulse, as long as high-energy carriers are continuously generated by one-photon absorption, free-carrier absorption, Auger processes, and multiphoton transitions.

In summary, we show by energy analysis of the electrons emitted by nonlinear photoemission processes that in silicon, at rather moderate fluences, an equilibrium electron population coexists with the primary photoexcited one. These populations have been selectively studied by varying the laser fluence and wavelength. The primary distribution reveals the existence of electrons at very high energies in the conduction band, generated by two- and three-quantum processes. On the other hand, the equilibri-

um distribution is described by a well-defined temperature which differs significantly from the lattice one during the excitation pulse. These results bring a new insight into the way carriers are photogenerated and thermalized in silicon under pulsed laser irradiation. Nonlinear photoemission shows unambiguously that multiquantum effects can be very efficient, in a spectral range where more conventional optical experiments are dominated by thermal effects.[14] This technique may then be a powerful spectroscopic tool in a range of wavelengths and fluences which cannot easily be studied by other means.

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