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Experimental Evidence of Two-Electron Transitions in Solids*

K. Betzler and T. Weller

Physikalisches Institut der Universität Stuttgart, D-7000 Stuttgart, Germany

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A new emission band at $h\nu = 2E_g$ is observed in Si using carrier injection in a p - n device. The extremely weak photon emission was detected by a special differential counting technique. From the photon energy, the quadratic dependence on the excitation intensity, and the weak temperature dependence, it is concluded that the observed emission is caused by a two-electron transition.

Two-electron transitions have been known for a long time in atomic physics as autoionization spectra. Heisenberg¹ has pointed out the selection rules for these transitions, $\Delta l_1 = \pm 1$ and $\Delta l_2 = 0, \pm 2$. In contrast to the situations in atoms, in solids it should be possible for both electrons to have the same initial state and the same final state. In the octahedral rotation group O , for example, two-electron transitions should be allowed from the Γ_4 or Γ_5 level to the Γ_1 , Γ_2 , Γ_3 , Γ_4 , or Γ_5 level.

To avoid frequency doubling of the one-electron transition by nonlinear optical effects, a crystal with inversion symmetry should be used. In this case two-electron transitions are forbidden because of the parity selection rule. In the space group, this selection rule does not hold. Therefore a crystal should be used in which at least one of the band extrema, i.e., the valence-band maximum or the conduction-band minimum, does not lie at the Γ point. In Si, which has O_h symmetry, the conduction-band minimum lies near the X point and the valence-band maximum is a Γ_5^+ state.² The different positions of these extrema in k space produces a weak one-electron transition because of momentum conservation, while the two-electron transition is permitted.

An additional advantage of this substance is the fact that it can easily be excited by injection when used as a p - n junction device.³ In absorption this effect cannot be observed because of the strong one-electron absorption at the energy $h\nu = 2E_g$.

Minority carriers in Si were generated in a cylinder of about 0.2 mm length and 0.2 mm diam by means of a forward-biased p - n junction. The recombination outside the junction region was investigated. Two types of diodes are investigated, with n - and with p -type bulk material. The resistivity of the bulk material was of the order of 1 Ω cm. Since the injection-current densities were very high (of the order of 10^4 A cm⁻²), experiments were performed with pulses of 22 μ sec length and at a duty cycle of 1%. The electric fields in the bulk region of the sample were less than 10^2 V cm⁻¹. The samples were mounted on a copper heat sink, whose temperature was controlled. From thermal conductivity data a temperature difference of less than 10°K between sample and heat sink was estimated.

The following experimental system was used to detect an extremely weak radiation at about twice the energy gap of Si (i.e., at a wavelength near 5600 Å). For registration of the signal, a

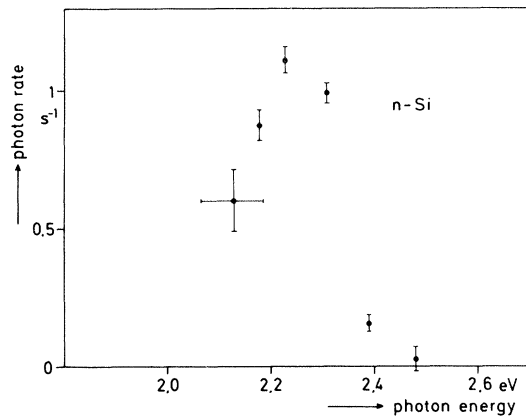


FIG. 1. Dependence of registered photon rate on photon energy. Injection current was 10.5 A; pulse duration, 22 μ sec; duty cycle, 1%. Temperature was 77°K.

correlating counting technique was used. The radiation was detected with a cooled EMI 6256A photomultiplier by counting individual electrical pulses. The dark count rate of the photomultiplier was about one pulse per second. The trigger level was optimized by use of a pulse-height analyzer. For effect registration, only the pulse rate was counted while the injection pulse was on. In between injection pulses, the dark pulses were counted. The simultaneous registration of the zero effect eliminates any drift effects. This measuring technique is essentially a digital boxcar integration and allows the detection of extremely weak light signals. It is superior to conventional analog boxcar integration because of an arbitrary duty cycle and an arbitrary integration time. For example, 10^{-19} W can be detected at an effective integration time of 15 min with the digital boxcar method. Because of the high sensitivity of the system, a Zeiss model MM 12 double monochromator had to be used in connection with a completely metal-enclosed cryostat system.

Figure 1 shows the energy dependence of the emission intensity at a temperature of 77°K. An emission peak is observed at about 2.25 eV. This new emission at about twice the energy gap of Si ($E_g = 1.12$ eV) was observed in several samples (*n*- and *p*-type material). Since the intensity of the new emission band was extremely weak, no better spectral resolution than that indicated in Fig. 1 could be obtained. Within the measurement accuracy, the bandwidth is twice that of the one-electron transition of about 0.05 eV,³ as is to be expected.

Figure 2 shows the dependence of the integrated

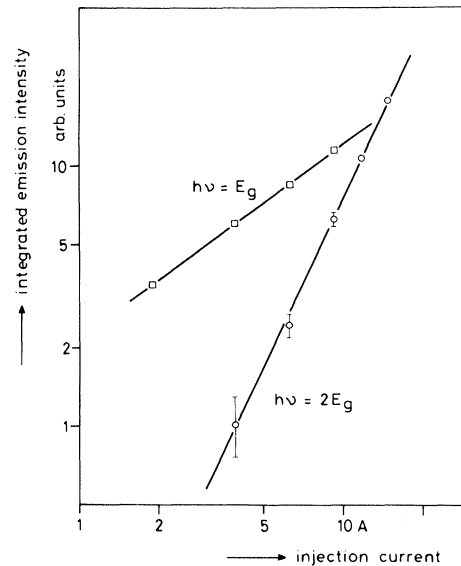


FIG. 2. Dependence of the integrated intensity of the emission band at $h\nu = 2E_g$ on injection current, compared on a different scale with the intensity of the one-electron transition at $h\nu = E_g$ at 290°K. Other data were the same as in Fig. 1.

intensity on the injection current of the emission band at $h\nu = 2E_g$ compared with the one-electron transition at $h\nu = E_g$. The intensity of the new emission band at $2E_g$ increases nearly quadratically ($\propto j^{2.1}$) with current density j , whereas in the case of $h\nu = E_g$ a nearly linear increase is observed. This suggests that the new emission is associated with the simultaneous transition of two electrons. For the two-electron transition the experimental data of Fig. 2 yield a very rough estimate of the transition probability whose value is 10^{-63} cm⁹ sec⁻¹ (photons per unit time, and volume per square of electron density in the conduction band and per square of defect-electron density in the valence band). For this estimate, a carrier density was obtained from the injection-current density and the lifetime. Also a calibrated count rate and values for reabsorption losses were used.

Furthermore, the temperature dependence of the integrated intensity of the $h\nu = 2E_g$ emission band was measured. Within the experimental accuracy (about 10%) the intensity was independent of temperature in the range between 290 and 370°K. Also the 77°K value agreed with the room-temperature value. This demonstrates that the new emission band is not correlated by a Boltzmann factor with the $h\nu = E_g$ emission.

A luminescence from semiconductors well above the energy gap is known in the case of ava-

lanche breakdown at high electrical fields,⁴ in the case of nonlinear optical effects,⁵ and in the case of Auger recombination.⁶ In this work, a new type of luminescence from Si is observed which cannot be explained by any of these effects. (1) For high-energy photon emission associated with avalanche breakdown, a field of about 10^5 V cm⁻¹ is needed at room temperature in Si, whereas in our case the field is of the order of 10^2 V cm⁻¹. (2) Frequency doubling of the usual band-to-band luminescence due to nonlinear optical effects can be excluded, since Si has inversion symmetry. Even if inversion symmetry should be violated by the electrical field, in our experiments the field was very weak compared with typical Stark-effect fields. Furthermore, in that case the luminescent intensity should depend on the cube of the injection current, since the extent of failure of inversion symmetry is proportional to the field. (3) Auger recombination followed by a radiative recombination from higher-lying conduction-band or valence-band extrema, as observed in Ge,⁶ can be excluded since there is no such extremum in Si.²

The proposed two-electron transition yields an emission energy at twice the energy gap and also describes the quadratic intensity-current dependence of Fig. 2. In contrast to the usual band-to-band luminescence in Si, this process needs no phonon for momentum conservation. The process may be described in the static one-electron

approximation using second-order perturbation theory. In this model, one perturbation operator is the Coulomb interaction between two electrons and the second is the electric dipole operator. The initial state is described as a Slater determinant of two conduction-band electrons in opposite *X* minima; the final state is described as that of two valence-band electrons at Γ . The intermediate state is composed of one valence-band electron at Γ and one conduction-band electron also at Γ . If this explanation is correct, excitonic molecules should also recombine in this way, emitting a single photon by total annihilation. Experiments to investigate this at liquid-He temperature are in progress.

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Raman Spectra of Amorphous Si and Related Tetrahedrally Bonded Semiconductors

J. E. Smith, Jr., M. H. Brodsky, B. L. Crowder, and M. I. Nathan
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

and

A. Pinczuk*

University of Pennsylvania, Philadelphia, Pennsylvania 19104

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Raman scattering has been studied in the amorphous form of Si and several related, tetrahedrally bonded semiconductors (Ge, GaAs, GaP, InSb). All vibrational modes of the material can take part in the scattering process, and the Raman spectrum is a measure of the density of vibrational states. The amorphous phases are found to have vibrational spectra very similar to the corresponding crystals, reflecting the similarity in short-range order of the two phases.

We have observed Raman scattering in amorphous Si and several related tetrahedrally bonded amorphous semiconductors. In an amorphous material all vibrational modes can contribute to the first-order Raman scattering,¹ in contrast to

a crystal, where only certain phonons near the zone center take part. The spectrum of an amorphous material is, then, a measure of the density of vibrational states. We compare the densities of vibrational states of the crystalline and amor-