EXCITATION MECHANISM OF LUMINESCENCE IN CdS BY VERY LOW-ENERGY ELECTRONS

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(Received 29 December 1969)

It is shown that low-energy electrons (<40 eV) excite luminescence in CdS at ~80°K by direct electron-hole pair production. Momentum in pair production is conserved without phonon participation.

The process of cathodoluminescence, in spite of its technological importance, has received little fundamental study.[1] It is a cascade process in which the energy of the primary electron is lost to smaller and smaller energy excitations. It has been suggested[2] that high-energy electrons lose energy predominantly to valence-electron plasmons[3] which, in turn, decay into one or more electron-hole pairs. On the other hand, high-energy electrons could produce electron-hole pairs directly without first exciting plasmons. In either case, we will observe electrons and holes of low energy (<50 eV), whether they are produced directly by an energetic electron or by the decay of a plasmon. The efficiency with which luminescence is produced in CdS at 80°K by electrons of 0-40 eV energy is the subject of the present study. In CdS, at 80°K, light is emitted when a free electron recombines with a bound hole.[4] The results of this experiment indicate strongly that the light is produced by individual pair-production processes in which momentum is conserved without phonon participation.

In this experiment, an atomically clean single-crystal surface of CdS at ~80°K was bombarded with electrons of 0-40 eV energy. The luminescent intensity and the electron current were recorded as a function of electron energy. The clean surface of CdS was produced by cleaving a single crystal of CdS[5] at ~80°K in an oil-free vacuum of 1×10^{-9} Torr. The (1210) cleavage plane of 12×4 mm^2 area contained many steps. Electrons produced by an oxide cathode were focused electrostatically onto the crystal surface. The temperature of the cathode was reduced to the lowest possible value to diminish the evaporation rate of cathode material. Satisfactory operation was observed at 60% of the rated heater voltage. An aperture of 6×2.5 mm^2 size in front of the CdS crystal ensured that only the central part of the cleavage area was hit by electrons. By applying an appropriate bias voltage to this aperture, the secondary electron-emission coefficient of CdS could roughly be determined. The secondary-electron emission coefficient was smaller than 0.25 over the whole energy range investigated. Electron source and crystal were enclosed in a magnetic shielding.

Light emerging from the crystal at right angles to the electron beam was focused onto the entrance slit of a 0.5-m Bausch & Lomb spectrometer. With a resolution of ~1%, a green edge emission line[6] was selected. Light at the exit of the spectrometer was detected by an E.M.I. 9558Q photomultiplier. The current in the multiplier was measured with a Keithley 417 micro-microammeter. Photomultiplier and electron-beam current versus voltage were plotted on an x-y recorder.

It was found that the spectral distribution of the light was independent of the bombarding electron energy. The light intensity was proportional to the electron current. No surface-charging effects were found for freshly cleaved crystals. Surfaces exposed to the residual gas in the vacuum system for many hours showed both weak surface-charging effects and a substantial decrease in luminescent efficiency.

For freshly cleaved surfaces, current and light threshold were observed to coincide. A lowering of the work function of CdS to find the energy threshold to produce luminescence was attempted. From a second oxide cathode located close to the CdS surface, some cathode material (presumably Ba) was evaporated onto CdS. This treatment lowered the work function and, therefore, the current threshold by as much as 3 eV. The shape of the curves of luminescence versus voltage changed very little during this lowering of the work function except that the true luminescent threshold was revealed. The electron energy scale was fixed by taking the work function of the oxide cathode (1.2 ± 0.2 eV) into account. The cathode work function was determined by measuring in the same experimental setup the threshold to draw current to a freshly evaporated film of gold on stainless steel, whose work function is 5.40 eV.[7] Knowing the cathode work function, the contact potential Φ of freshly cleaved CdS

was determined from the threshold voltage to draw current to CdS. The value $\Phi = 4.8 \pm 0.3$ eV found in this experiment is in good agreement with the value $\Phi = 5.0$ eV of Ref. 7.

In Fig. 1 (top panel), the luminescent yield (number of photons per electron) is plotted versus electron energy. The bottom panel of Fig. 1 shows the luminescent power yield (number of photons per electron power absorbed by the crystal). The data represent one of three practically identical results from three different crystals. The electron energy is adjusted such that it indicates the energy of an electron above the conduction band of the bulk in CdS.[8]

Clearly evident in Fig. 1 (top) are (i) a sharp rise of the luminescent yield from a threshold at $\simeq$4 eV, (ii) a plateau from 6 to 8.5 eV, and (iii) a rise from 9 eV on. The threshold at 4 eV is interpreted as the threshold for single pair production. Under the assumption that energy and momentum are conserved without phonon participation in the electron-hole pair-production process, the threshold for this process is found to be at the energy[9] $E_t = E_g[1 + m/(m_e + m_h)]$, with E_g = energy gap of CdS = 2.5 eV; m = mass of the incoming electron; and m_e, m_h = masses of the excited electron and hole, respectively. For m = free electron mass, $m_e = 0.17m$, and $m_h = 0.81m$,[10] we find $E_t = 2E_g = 5$ eV, in fairly good agreement with our data. It is questionable whether one can use the free-electron mass for the incoming electron. On the basis of band-structure calculations,[11] however, no better values can be assigned to the effective mass of the incoming electron. The plateau from 6 to 8 eV is due to the fact that the incoming electron can produce at most one electron-hole pair. The increase in luminescent yield from 9 eV on is interpreted as being due to the creation of two or more electron-hole pairs in succession. The threshold for two-pair production is in good agreement with the value calculated according to Ref. 9 of $3.1E_g \simeq 8$ eV.

In Fig. 1 (bottom), the luminescent power efficiency displays the same features as the yield. The plateau in the yield curve has changed into a drop, whereas the thresholds for one- and two-pair production are still very well visible. In addition, we see that the power efficiency at 40 eV is ~30% larger compared with that at 15 eV. We expect a more efficient use of the energy available for pair production as the electron energy is increased beyond the threshold for creation of two pairs in succession. The high luminescent efficiency at ~5 eV is rather surprising. At such low energies, the mean free path for inelastic collisions is substantially larger than at higher energies.[12] For pairs created further away from the surface, the probability for nonradiative recombination at the surface[13] is smaller.

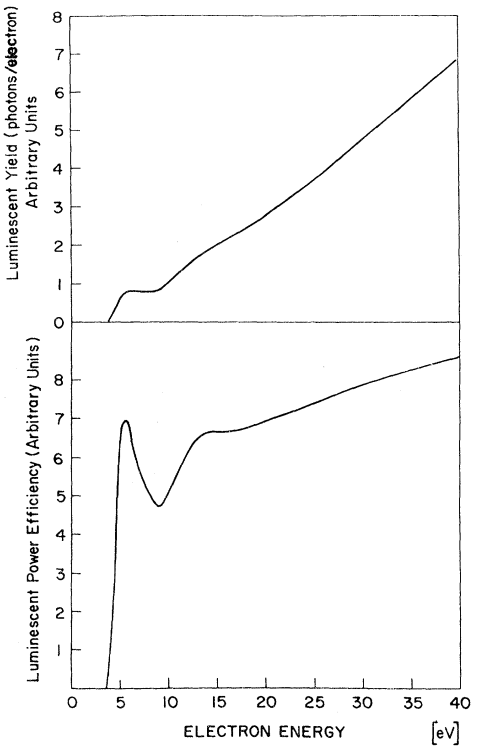

FIG. 1. The top panel shows the luminescent yield (photons per electron); the bottom panel, the luminescent power efficiency (photons per power absorbed) versus electron energy. The electron beam hits a single-crystal surface of CdS at ~80°K, cleaved in ultrahigh vacuum. Light is observed at a wavelength λ = 5230 Å.

Pair creation in semiconductors by low-energy electrons has been observed in avalanche breakdown,[14] enhanced quantum yield in photoexcitation,[15] and photoelectric emission.[16] All the data indicate that the threshold energy amounts to between two and three times the energy gap. These results suggest that energy and momentum conservation without phonon or impurity cooperation is, in general, required in pair creation.

The author would like to thank Dr. H. L. Stadler and Dr. L. C. Davis for many helpful discussions.

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INTERACTION OF DISLOCATIONS WITH ELECTRONS AND WITH PHONONS*

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The interaction parameter of moving dislocations with electrons and with phonons in aluminum was determined from measurements of ultrasonic attenuation changes with stress. The results indicate that the interaction with electrons is temperature independent and that the interaction with phonons increases with increasing temperature. These results are consistent with theoretical predictions.

In this note we report a new approach to measuring, by means of ultrasonic methods, the interaction of dislocations with electrons and with phonons in solids. (Specifically, we study the resistive force on a moving dislocation.) This method does not depend on a knowledge of the dislocation density and of other inaccurately known or difficult to determine features of the dislocation network. The main difficulties in obtaining reliable values for this interaction are thus eliminated. By using this method, the magnitude and temperature dependence of the interaction parameter (hereafter called B) were obtained in aluminum, in the temperature range $10°K \lesssim T \lesssim 250°K$.

Previous attempts to measure B by ultrasonic methods[1-3] required an independent determination of the dislocation density, thus involving a large uncertainty in the results. Other attempts were also made to obtain B from average dislocation velocity determined in mechanical tests.[4-6] A comparison of the values of B obtained with those derived from previous ultrasonic experiments was given by Fanti et al.[3] In the present approach, small changes in ultrasonic attenuation $\Delta\alpha$ are measured as a function of frequency. These changes result from the application of a small bias stress to the specimens during the experiment. From an analysis of this incremental attenuation it is possible to extract the value of B without knowing the dislocation density. In order for this analysis to be applicable the bias stress must be large enough to cause unpinning of dislocations from weak pinning points, but smaller than the stress required to generate new dislocations. Bias stresses in this range do not affect measurably the attenuation due to mechanisms other than dislocation vibrations. The measured $\Delta\alpha$ are, therefore, due entirely to the unpinning of dislocations with the resulting increase in the average loop length.

The analysis of the relation between $\Delta\alpha$ and B proceeds as follows. For the extensible string model of a vibrating dislocation, the total attenuation due to dislocations is given by[7]

$$\alpha(L_c) = \frac{4R\Lambda G b^2}{\pi^2 A} \frac{\omega^2 d}{(\omega_0^2 - \omega^2) + (\omega d)^2}, \qquad (1)$$