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Photoluminescence of CdSe: Evidence for selective etching of donor states

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Photoluminescence of *n*-type CdSe at 1.8 K and above is used to investigate the effect of photoelectrochemical etcing on the impurity distribution near the semiconductor surface. The results suggest that shallow donor states are removed from the surface preferentially, and hence the surface becomes relatively intrinsic following that surface treatment. The model of nonuniform charge flow is invoked to explain this phenomenon.

Control of semiconductor surfaces is an important tool for the fabrication of efficient and stable optoelectronic devices. Photoelectrochemical etching (photoetching) of III-V, II-VI, and other materials is known to yield surfaces with desirable properties for such applications.[1,2] Photoetching of II-VI compounds produces a unique morphology with an etch-pit density higher than 10^9 cm^{-2}. It was previously shown that this density depends on the donor density of such materials.[3] It was suggested that the etch-pit pattern is a manifestation of nonuniformities in the charge flow of semiconductor junctions due to the ionized impurities. Some evidence in support of this hypothesis was found.[4,5]

The photoluminescence (PL) of CdSe has been investigated by a number of groups in the past.[6-10] At low temperatures (4.2 K) the main emission lines were shown to consist of free and bound excitons and of donor-acceptor pairs with their respective LO-phonon replica.[6] In the present work high-resolution photoluminescence (PL) at 1.8 K and above is used to probe directly the signals which are associated with donor states and changes in these signals which are induced by photoetching. Thus direct evidence is advanced in support of the above hypothesis.

Photoluminescence was measured with a Jobin-Yvon monochromator (model no. HRD). The excitation source was an argon-ion laser (Coherent model no. INNOVA 15 W). The temperature was controlled (to 0.01 °C) using an SMC cryogenic Dewar. Oriented (0001) CdSe crystals were purchased from Cleveland Crystals Inc. They were polished down to 0.3-μm grit and then chemically etched with a 1:4 HNo_3-HCl mixture (aqua regia). The crystals were photoetched in 1*M* $HClO_4$ solution. They were immersed for 10 min in 10% KCN solution to remove elemental selenium which was produced during both chemical etching and photoetching.

The PL spectrum of the chemically etched crystals exhibited the known features; among them the two main peaks were the donor-bound exciton (I_{2A}) at 1.8217 eV and the donor-acceptor peak (at 1.7305 eV) with its LO-phonon replica.[7] Increasing the light intensity by 3 orders of magnitude led to a blue shift of only 4 meV in the position of the donor-acceptor peak. This result is consistent with the theory of Neumark *et al.*[11] as is also shown in Fig. 1. In this figure the position of this peak, as predicted by this theory is drawn as a function of the normalized light intensity for different donor densities. The experi-

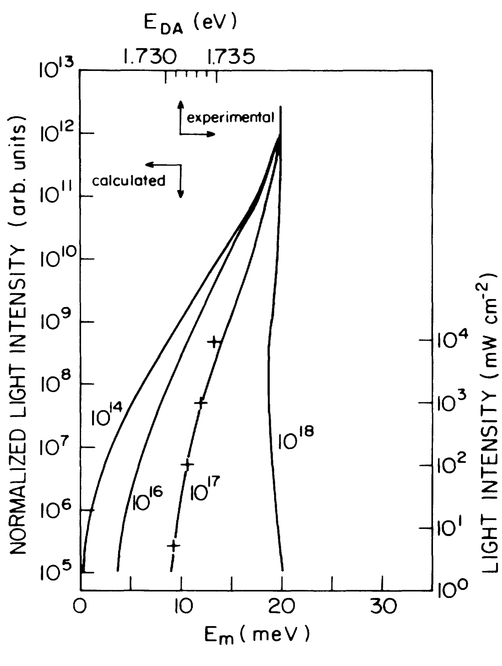

FIG. 1. Calculated (—) and measured (+) shifts for the donor-acceptor peak photoluminescence spectra of a chemically etched CdSe [(0001) 1 Ohm cm] at 1.8 K. Excitation wavelength is 5154 Å. Bohr radius of the impurity was taken as 40 Å in the calculations.

mental points were fitted to the theoretical curves. A satisfactory agreement with the calculated curve was obtained only for $N_d = 10^{17}$ cm^{-3} which is somewhat higher than the nominal donor density calculated from the known resistivity of the crystal ($> 10^{16}$ cm^{-3}).

The position of the donor-acceptor peak for crystals with different resistivity values is given in Table I. The donor-acceptor peak exhibits a blue shift for lower nominal donor density (higher resistivity). Similar shifts were observed also at 77 K.[5]

The position of the donor-acceptor peak (E_{DA}) is given by Eq. (1).

$$E_{\mathrm{DA}} = E_g - E_D - E_A + q^2/\epsilon\epsilon_0 r_m \ . \tag{1}$$

Here E_g is the energy gap E_D and E_A are the position of the donor and acceptor levels, respectively, q is the elementary charge; $\epsilon\epsilon_0$ is the dielectric constant of the host crystal multiplied by the permittivity of free space, and r_m is the distance between the donor and acceptor pairs which produce the strongest luminescence center.

From the theory of Neumark *et al.*[11] one expects that an increase in the donor density would lead to a blue shift in the position of the donor-acceptor peak since the mean distance between such pairs and consequently r_m decreases as the donor density increases. However it is well known that an increase in the donor density leads also to a shrinkage of the fundamental energy gap (E_g).[12] Hence the combined effect may result in either a blue or a red shift depending on which effect is dominant. Indeed the bound exciton exhibits a red shift of 4 meV when the resistivity decreases from 11 to 0.3 Ω cm. This shift can be attributed to the shrinkage in the energy gap as a result of the increase in the donor density. However the red shift in the donor-acceptor peak position is 27 meV and is too large to be explained by that effect only.

A similar problem was addressed by Neumark *et al.*[11] who suggested the presence of two kinds of donors in ZnSe, one due to Na_i the other due to a group-III element, the former being a more shallow one. It is suggested therefore that Na(Li) metal impurities are introduced into the crystal matrix during growth leading to a donor-acceptor pair of the type Li_i-$\mathrm{Li}_{\mathrm{Cd}}$. Thus crystals with lower resistivity (typically grown under a higher vapor pressure of Cd incorporate a larger concentration of selenium vacancies which serve as shallow donors. These crystals exhibit a smaller degree of compensation (produced by the Li atoms) and a red shift in the donor-acceptor peak position. Indeed a more recent study of CdSe crystals[13] shows that the photoluminescence spectrum of quasicompensated crystals consists of two separate donor-acceptor peaks, one of which is observed also in the present crystals at 1.73 eV, the other at a higher energy (1.77 eV). A similar observation was obtained in thin-film CdSe which was prepared by vapor deposition and exhibits a larger degree of compensation as determined by Hall measurements. Thus the 1.77-eV peak can be associated with alkali-metal impurities in the CdSe lattice.

TABLE I. Position of the donor-acceptor photoluminescence peak for CdSe at 1.8 K. Excitation intensity is 5.7 mW cm^{-2}.

Resistivity (Ohm cm)	Donor-acceptor peak position (eV)
11	1.7556
1	1.7306
0.3	1.7289

Secondary-ion mass spectrometry (SIMS) measurements of CdSe crystals, similar to the ones used throughout this study, show sodium as one of the major impurities in the crystal.

The PL of the photoetched crystals was remarkably different from that of the chemically etched ones as shown in Fig. 2. The intensity of the luminescence is weaker here. The spectrum consists now mainly of a broad peak and the bound (to donor) exciton I_{2A}. Both peaks exhibit a very strong dependence on the excitation intensity. Under the lowest intensity the broad peak (1.738 eV), and its LO replica resemble the previously observed donor-acceptor peak (1.7305 eV) although it is shifted to the blue. This observation suggests that the donor density of the CdSe crystal decreased after photoetching (see Table I). However at higher light intensities the broad peak exhibits an appreciable blue shift of almost 50 meV. This shift clearly shows that under strong light intensity the donor-acceptor peak is saturated and a new recombination mode becomes effective. Hence it can be assumed that the broad peak obtained after photoetching is actually a superposition of two peaks which can be deconvoluted by using either a very low or a very high excitation intensity. In addition, as the light intensity is increased the donor-bound exciton peak gradually disappears. These results are consistent with the hypothesis that the donor density at the CdSe surface decreases after photoetching.[4,5] It was found[14] that under strong excitation the donor-acceptor peak is saturated and a peak due to a transition from a bound-state directly into one of the bands (the so-

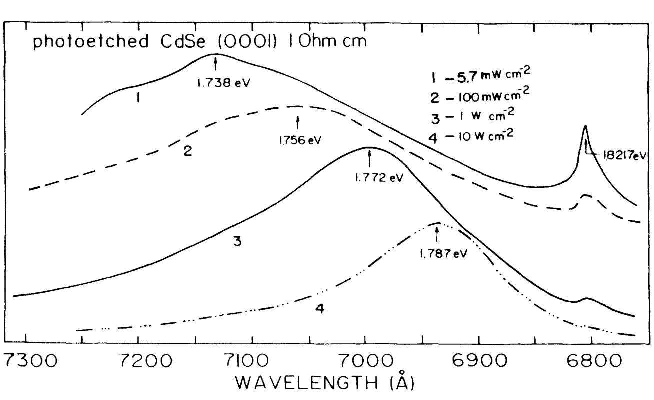

FIG. 2. Photoluminescence spectra of photoetched CdSe at various light intensities. The excitation wavelength is 5145 Å; $T = 1.8$ K. Note the large blue shift of the peak position with increasing light intensities.

called free-to-bound transition) is observed. Thus the new peak (at 1.787 eV) in the photoetched crystal could be ascribed to a recombination of an electron in the conduction band with a hole in some unspecified acceptor state. Alternatively this peak can be associated with a donor-acceptor transition of the type Li_i-Li_{Cd} which was discussed previously. The radius of the electron (bound to the donor) is smaller in this case[11] and hence the peak position is expected to exhibit an appreciable blue shift with increasing light intensity.

Since Li diffuses rather easily through the crystal matrix during the crystal growth it is expected that the average distance between donors and acceptors of this kind will be smaller due to the Coulombic interaction.[15] Consequently this transition appears at higher energies[15] and more important the process of photoetching is rather noneffective in removing those donors (Li_i) because they behave like a neutral entity (together with the associated acceptor Li_{Cd}) which does not distort the electric field in its neighborhood (see below).

Using shorter wavelengths for the excitation, light is absorbed closer to the surface and hence the effect of the photoetching is further accentuated as shown by Fig. 3. It is observed that the excitonic peak gradually disappears when the excitation wavelength is decreased. In addition the main PL peak exhibits a blue shift with decreasing wavelength of the excitation source, consistent with a more pronounced effect of the photoetching near the semiconductor effect.

The two main peaks of the PL spectra, i.e., the band-to-band (or excitonic) and the donor-acceptor peaks were resolved also at 77 K under the lowest excitation intensity (5.7 $\mathrm{mW\,cm^{-2}}$). Both peaks exhibited a blue shift after photoetching as would be anticipated for a material with a lower density of donors.[5]

These data show that after photoetching, the density of the donors at the semiconductor surface, has diminished. Although the exact nature of the new peak (at 1.787 eV) is yet unknown the present results suggest that it might be associated with a compensating donor-acceptor pair such as Li(Na) which diffuses into the crystal during its growth.

Thus the photoetching of II-VI compounds leads to a profile of donors which is desirable for optoelectronic devices and hence it is not surprising that their performance is improved remarkably following that surface treatment. The mechanism of the etching of donors at the semiconductor surface by photoetching was discussed in detail in the past[3-5] and is believed to be related to nonuniform currents at semiconductor junctions. The positively charged impurities (for n-type semiconductors) exert very strong nonuniform electric fields near the surface. These fields produce nonuniform flow of charge carriers. The photocurrent density is higher near the ionized impurities so that the rate of photoetching near those impurities is larger. Hence the surface becomes relatively poor in donors after photoetching and the surface morphology which is produced by photoetching is highly nonuniform.

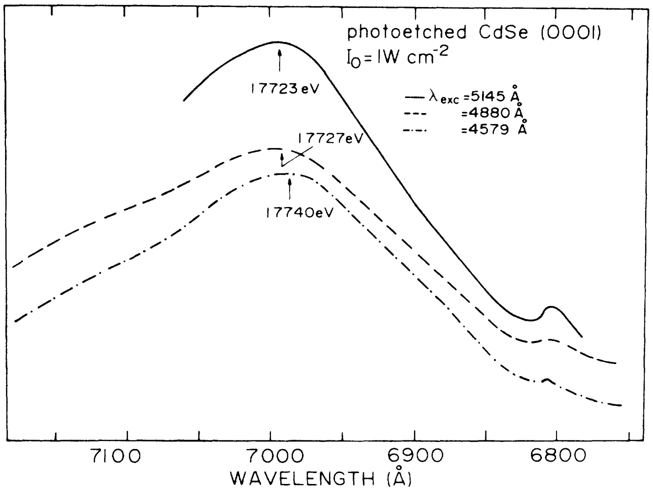

FIG. 3. Dependence of the PL spectra of photoetched CdSe on the excitation wavelength. $T=1.8$ K.

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