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Photoluminescence of CdSe: The effect of photoetching

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The photoetching of single crystal *n*-type CdSe was investigated, using photoluminescence at room temperature and at 77 K. A blue shift is observed in the photoluminescence spectrum of crystals when the doping density is decreased. It is explained through the decrease in density of bound excitons and donor-acceptor pairs when the impurity concentration decreases. A similar blue shift is observed for crystals which were photoetched and is attributed to the preferential etching of dopant atoms (vacancies) near the semiconductor surface. This observation is supported by the dependence of the photoluminescence on the electrode potential. Consequences of our findings on the performance and stability of photovoltaic (photoelectrochemical) cells are discussed.

INTRODUCTION

Photoluminescence (PL) has been used extensively in the past for the characterization of semiconductors, and semiconductor-electrolyte interfaces.[1-5] The luminescence spectrum of CdSe which consists of bound and free excitons as well as donor-acceptor pairs was fully resolved at 4.2 K only.[5] The potential dependence of the PL at the CdSe-polysulfide interface obeys the "dead-layer" model[6-9] at forward (cathodic) potentials exceeding -0.2 V.[4] Close to short-circuit conditions, a pronounced PL peak was observed;[4] its origin is not yet understood.

Photoelectrochemical etching of the CdSe leads to a considerable improvement in the *I-V* characteristics of photoelectrochemical cells based on this semiconductor.[10] It is also interesting that the surface of photoetched CdSe contains a pattern of small and highly dense ($>10^9$ cm^{-2}) etch pits as in Fig. 1. It was recently shown that the density of the etch pits varies with the doping density of the semiconductor.[11] To account for these results, as well as for others, we have suggested recently[12,13] that donor states are preferentially etched from near the semiconductor surface during photoetching. Photoluminescence is particularly useful for investigating this phenomenon since it is less sensitive to surface irregularities than capacitance or electrolyte electroreflectance.

In this work we have studied the photoluminescence of CdSe crystals with carrier concentrations varying between

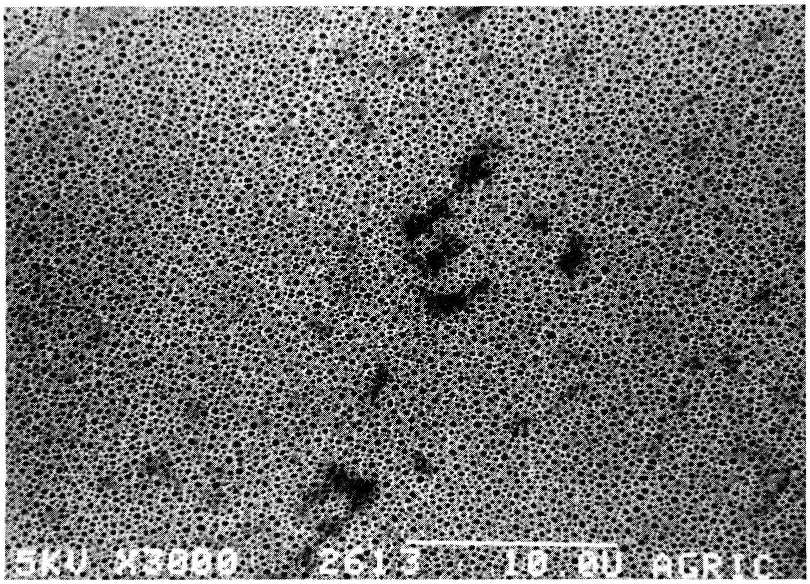

FIG. 1. Scanning electron microscope picture (10 000×) of photoetched CdSe.

10^{15} and 10^{17} cm^{-3}. Strong evidence is brought forward that photoelectrochemical etching of the crystal leads to a preferential etching of dopant atoms near the semiconductor surface. In the Discussion we argue that such preferential etching of dopant atoms may lead to improved photoelectrochemical (photovoltaic) properties of the semiconductor electrode.

EXPERIMENT

CdSe crystals with nominal resistivity values of 0.1, 1, and 10 Ω cm were purchased from Cleveland Crystals, Inc. In all of the crystals, the face perpendicular to the *c* axis [(0001) plane] was exposed to the light. The crystals were polished with alumina suspension (Linde) down to 1 μm; etched with a (1:4, volume ratio) HNO_3-HCl mixture (aqua regia). They were immersed in 10 wt. % KCN solution for a few minutes. Photoetching was performed in the aqua-regia mixture which was diluted three to five times. A reverse bias of 1.0 V relative to standard calomel electrode (SCE) was applied for 1—2 sec. After photoetching the electrode was immersed in a hot (70 K) 10 wt. % KCN solution for 1—2 min to dissolve the elemental selenium formed during photoetching (and etching). The polysulfide solution was prepared by dissolving (1 *M* of each) the three components—Na_2S, S, and NaOH—in deionized water.

The luminescence system is described in detail elsewhere.[5] It consisted of a Coherent Ar-ion laser (excitation wavelength of 5145 Å), a Spex model No. 14018 double-path monochromator, and an RCA model No. 31034 cooled photomultiplier.

RESULTS

Figure 1 shows a scanning electron micrograph of a photoetched CdSe electrode. In contrast with a chemically etched CdSe the photoetched surface is highly corrugated with density of etch pits exceeding 10^9 cm^{-2}. Recently, the density of etch pits was shown to depend strongly on the doping density[11] (see Discussion for further details). Figure 2 shows the *I*-*V* curve of an illuminated CdSe electrode, in polysulfide electrolyte, prior to and after photoetching. The improvement in the short-circuit current can be attributed to the reduced reflectivity of the surface.[14] However, the larger improvement in the photocurrent near the point of maximum power, after photoetching, can be explained by preferential etching of recombination centers near the semiconductor surface or alternatively through improved charge-transfer kinetics resulting from the surface corrugation. Figure 3 shows the photoluminescence spectrum of two CdSe crystals in a photoelectrochemical cell containing a (1;1;1) polysulfide solution (1 M with respect to Na_2S, S, and NaOH). The spectrum was not affected by the variation of the excitation wavelength. It is not possible to discriminate between the various contributions to that peak but a recent report[4] suggests that it consists of donor-acceptor pairs and bound- and free-exciton contributions. The salient feature in this figure is the blue-shift of the peak maximum for the lower-density (10 Ω cm) electrode. If the luminescence of bound excitons or donor-acceptor pairs is predominant, such a shift is not unexpected, since the more abundant the dopant atoms (vacancies), the more impurity-induced excitation centers (IC) exist and consequently a red-shift in the luminescence spectrum occurs. We failed to observe a significant shift in the luminescence spectrum of photoetched CdSe as compared to the etched surface at room temperature.

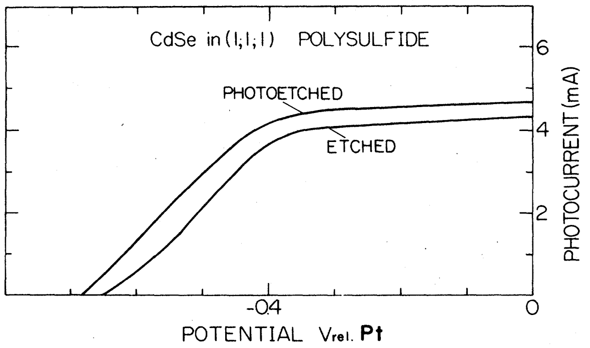

FIG. 2. *I*-*V* curve of CdSe in (1;1;1) polysulfide (1*M* with respect to NaOH, Na_2S, and S) prior to and after photoetching.

The potential dependence of the luminescence of CdSe in the polysulfide electrolyte conforms to the dead-layer model for cathodic (forward) potentials more negative than -0.2 V relative to the Pt.[4] According to that model, the intensity of luminescence (I_f) at a given wavelength is given by

$$I_f = I_0 \phi e^{-\alpha W} , \tag{1}$$

where ϕ is the quantum efficiency of luminescence at flat-band conditions; I_0 is the intensity of the incident light; α is the absorption coefficient; and *W*, the thickness of the space charge layer is

$$W = \left[\frac{2\epsilon_0 \epsilon}{e N_d} \right]^{1/2} (V - V_{FB})^{1/2} . \tag{2}$$

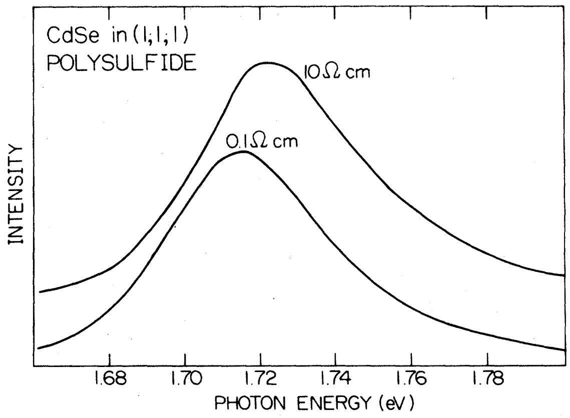

FIG. 3. Photoluminescence of two CdSe crystals with different doping densities (resistivities) in (1;1;1) polysulfide. Potential was -0.6 V relative to the Pt electrode, i.e., -1.35 V relative to the standard calomel electrode.

In Eq. (2), V and V_{FB} are the applied potential and flat-band potential, ϵ_0 is the permittivity of free space, ϵ is the dielectric constant, N_d is the doping density, and e is the electric charge of the electron. The flat-band potential of CdSe in (1;1;1) solution of polysulfide was taken as -0.78 V relative to the Pt electrode (i.e., -0.78 V cathodic of the reduction-oxidation potential of the solutions which is itself -0.75 V relative to the calomel electrode).[14] Plotting now $\ln I_f$ versus $(V-V_{\mathrm{FB}})^{1/2}$ we obtain in Fig. 4 a linear curve. The doping density is obtained from the slope by using the values $\alpha = 1.04\times10^{7}$ m^{-1} ($\lambda = 514.5$ nm), $\epsilon_0 = 8.85\times10^{-12}$ C^{2}m^{-2} N^{-1}, $\epsilon = 10.6$, $e = 1.6\times10^{-19}$ C. Thus, the doping density of the CdSe crystal falls from 2.3×10^{15} to 1.44×10^{15} cm^{-3} after the first photoetching and to 1.27×10^{15} cm^{-3} after a second photoetching. The nominal resistivity of this crystal is 10 Ω cm. Taking the value of 650 cm^2 sec^{-1}V^{-1} for the electron mobility in CdSe,[15] one obtains a value of 0.96×10^{15} cm^{-3} as the nominal doping density which is in fair agreement with the value obtained from the

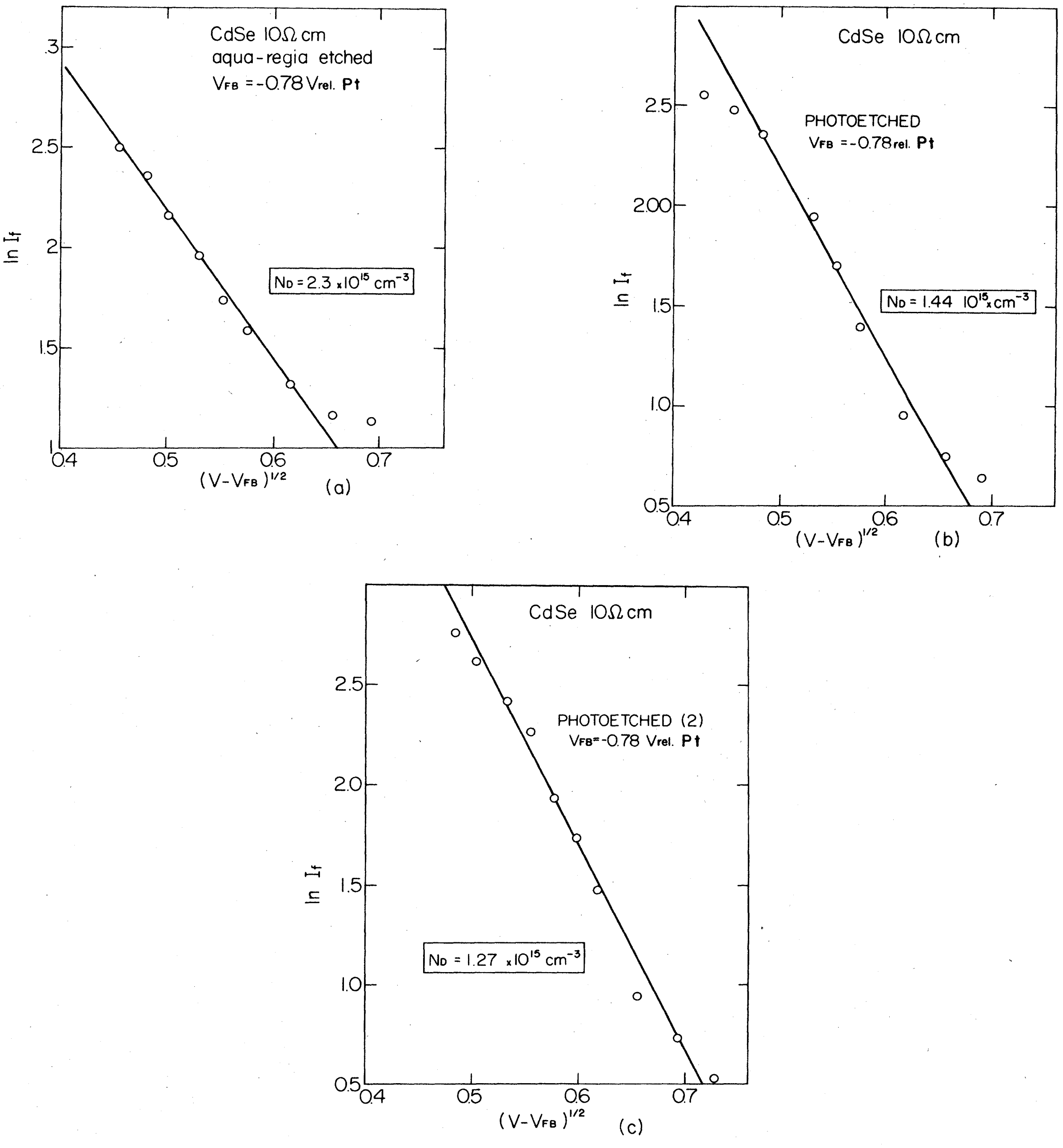

FIG. 4. Plot of ln(photoluminescence intensity) vs (potential − flat band potential)$^{1/2}$ for chemically etched (a) and photoetched (b) and (c) CdSe in (1;1;1) polysulfide. The doping density which is obtained from that slope decreases after photoetching.

luminescence data for etched CdSe. The doping density obtained with this technique agreed within a factor of 2—3 with the nominal values for all three crystals. Reduction in the calculated doping density after photoetching was common to all crystals. Therefore *in situ* photoluminescence experiments clearly show that the doping density of photoetched CdSe is reduced near the surface.

Further evidence for that observation is obtained from low-temperature (77 K) luminescence experiments which are shown in Figs. 5—7. Figure 5 shows the photoluminescence spectrum of two CdSe crystals with nominal resistivities of 0.1 and 10 Ω cm. The spectrum of the lower doped material exhibits two peaks at 1.811 and 1.817 eV.[5] This spectrum is similar to that reported previously and reflects partial resolution of the contribution from the IC and that of the free excitons. The spectrum of the heavily doped CdSe is dominated by the IC. The relatively small red-shift (4 meV) of the IC peak, in the heavily doped material is not unexpected since the density of IC increases with doping density. Figure 6(a) shows the photoluminescence spectra of a lightly doped CdSe prior to and after photoetching. A blue-shift of the IC peak ($\sim$2 meV) is clearly exhibited and it indicates that the number of IC decreased after photoetching as expected. Also interesting is the observation that the free-exciton peak disappears after photoetching of the lower doping material. The blue-shift in the luminescence spectrum is exhibited also by the highly doped material after photoetching as Fig. 6(b) shows. Finally, Fig. 7 shows that even after photoetching the blue-shift of the lightly doped CdSe persists and reflects the differences in doping density of the two photoetched crystals.

A few comments are in order now. Firstly, in all experiments done throughout the entire work, the light intensity was kept very weak in order to avoid complications due to light-induced corrosion or creation of electron-hole plasma. No spectral shifts were obtained when the light intensity was increased by up to 1 order of magnitude. Also no spectral changes were found by varying the exci-

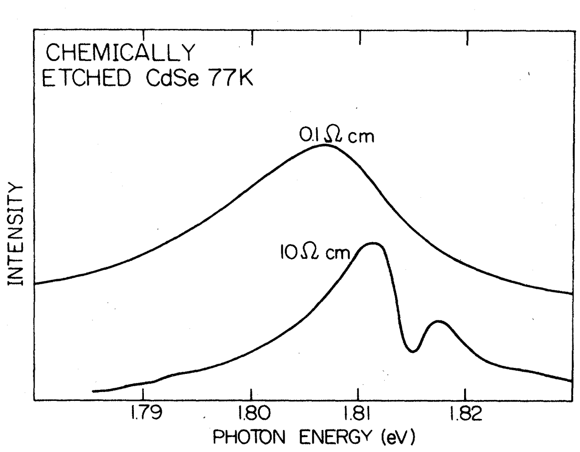

FIG. 5. Photoluminescence spectrum of chemically etched CdSe in 88 K. Note the blue-shift in the spectrum of the lowly doped crystal.

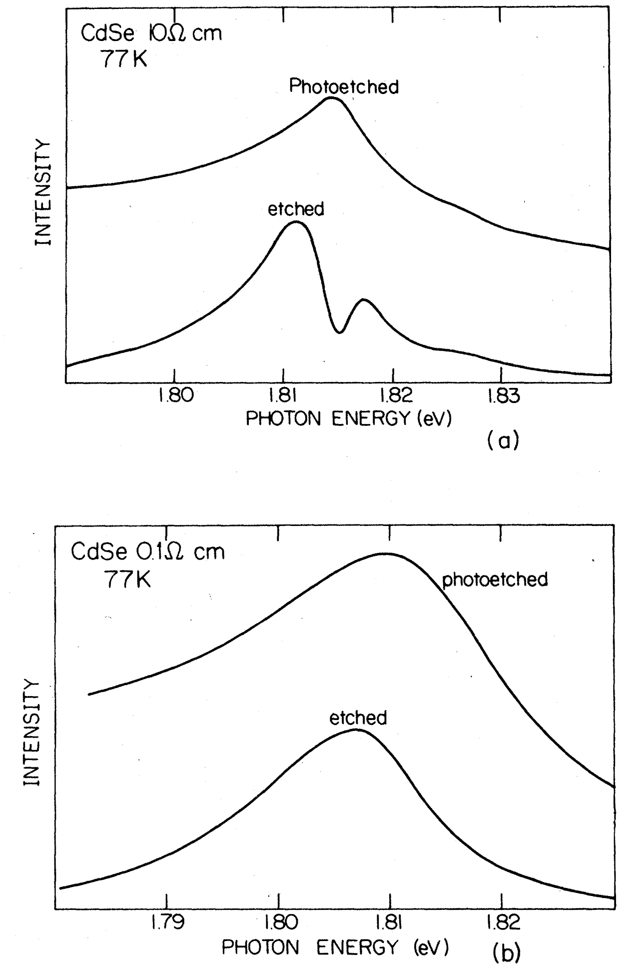

FIG. 6. Photoluminescence spectrum of a CdSe crystal exhibits a blue-shift after photoetching (i.e., effective lower doping density). (a) 10-Ω cm electrode; (b) 0.1-Ω cm electrode. Note that the absolute luminescence intensity of the photoetched crystal is smaller than that of the etched crystal (compare also Fig. 4).

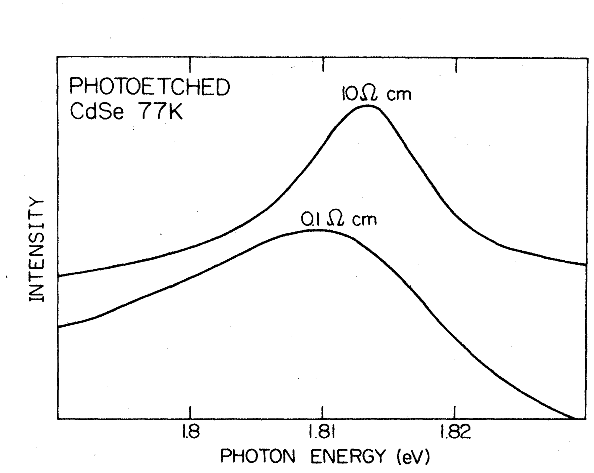

FIG. 7. Photoluminescence spectrum of photoetched CdSe at 77 K with two nominal resistivities.

tation wavelength or by using different etching procedures other than photoetching.

It is also interesting to note that III-V compounds tend to show a red-shift in their luminescence spectrum when the doping density is decreased. This is because luminescence due to band-to-band recombination predominates there and in this case the Burstein-Moss effect applies (see the Discussion). Increased self-absorption in the photoetched samples should have shifted the spectra in the opposite direction, nevertheless, the degree of self-absorption and its effects on the reported results are under active investigation. Hence, our results clearly indicate that the doping density of CdSe near the surface decreases after photoetching.

DISCUSSION

Indications for preferential etching of dopat atoms were obtained previously with ZnSe electrodes.[13] Following photoetching, a red-shift in the photocurrent spectrum was observed. This shift was analyzed using the Burstein-Moss model for heavily doped semiconductors. This model is based on the idea that in heavily doped semiconductors electrons occupy the lower energy states in the conduction band and hence these states are not accessible to the photoexcited electrons. Consequently the absorption spectrum suffers a red-shift with decreasing doping density. Using this model one can attribute the red-shift in the photocurrent spectrum of photoetched semiconductors as emanating from the lower doping density near the semiconductor surface.[16] Also, the slope of the (photocurrent) versus potential curve indicated a lower doping density of photoetched ZnSe. Red-shifts in the photocurrent spectrum were observed with photoetched Cd(Se,Te) semiconductors[17] as well. It is therefore expected that a process which involves band-to-band excitation (photocurrent spectrum) will suffer a red-shift after photoetching, whereas recombination through impurity centers will show a blue-shift (see also Ref. 18 for the effect of impurity on bound exciton luminescence).

Photoetching of semiconductor surfaces may affect the performance of a photoelectrochemical (photovoltaic) cells through a number of reasons: It first leads to a texturing of the surface which reduces the surface reflectivity. The textured morphology leads also to improved charge-transfer kinetics, hence to a decreased rate of recombination in phootelectrochemical cells. This effect is important under concentrated light but is probably rather of minor importance under terrestrial insolation. Contrarily corrugated morphology increases the leakage (dark) current of a device and as such can be counter productive.

Electron microscopy and cathodoluminescence measurements[10,19] established that grain boundaries, material defects and dislocations are preferentially etched from the semiconductor surface during photoetching. Naturally, this effect alone could bring about a significant improvement in the cell performance especially for highly damaged surfaces.[20,21]

Recent experiments with heavily doped [10^{18} cm^{-3} ZnSe (Ref. 22)] show that the doping density fell by as much as 1 order of magnitude, near the semiconductor surface, after photoetching. Chemical etching, on the other hand, did not lead to any change in the measured doping density at the semiconductor surface as could be inferred from Hall-effect, capacity, and photoluminescence measurements.

The advantage in having an interface with a dopant profile of the form $n^+ \mid n \mid$ electrolyte (metal) is multiple and is well established for high performance photovoltaic cells.[21] First, the n^+ bulk serves as a mirror which reflects outdiffusing holes back into the interface. In addition, the reduced doping density on the surface (n) leads to a thicker space-charge layer and consequently to a lower rate for the bulk recombinations. Finally, dopant atoms serve as recombination centers, and their elimination from near the surface decreases (near) surface recombination. Thus, photoetching of semiconductors leads to an improved performance of photoelectrochemical and photovoltaic cells by establishing such a dopant profile. Improvement in cell stability which is always observed after photoetching[12] can be explained by the more uniform distribution of photocurrent after photoetching, in addition to the higher surface corrugation.

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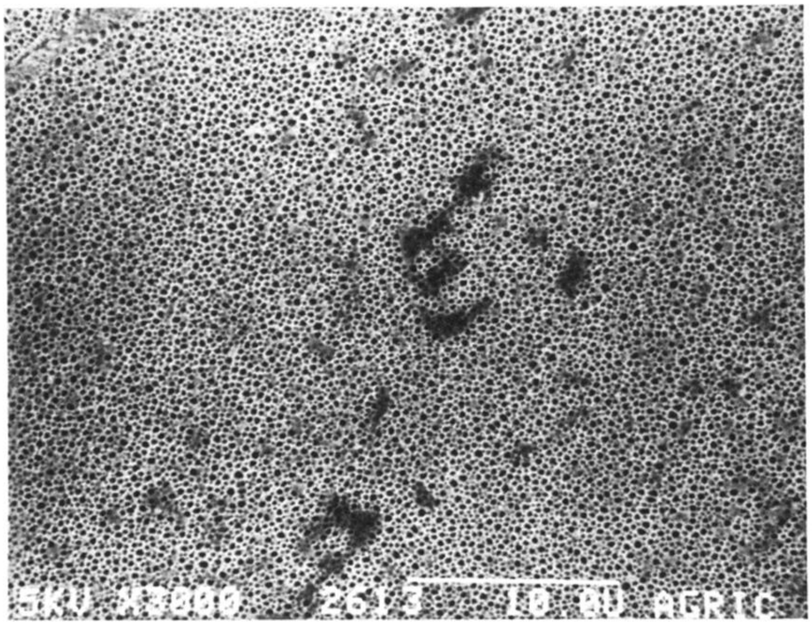

FIG. 1. Scanning electron microscope picture (10 000×) of photoetched CdSe.