# Photoelectrochemical Etching of ZnS: Further Evidence for Non-Uniform Flow of Charge Carriers in Schottky Barriers

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**Abstract.** It is shown that short photoelectrochemical etching of two kinds of ZnS crystals leads to a reduction in the surface recombination velocity as evidenced by their increased photocurrent. The unique surface morphology ($> 10^9$ pits $cm^{-2}$) revealed after photoetching supports the hypothesis that the charge flow within the space charge layer is highly non-uniform.

Zn-chalcogenides are wide bandgap semiconductors which are studied intensively for light emitting diodes [1–3] and electroluminescing devices [4, 5]. The output of such devices is determined to some extent, if not mostly, by recombination processes which take place at the semiconductor surface. This is common also for other electro-optical devices such as photovoltaic and photoelectrochemical cells. The quantum efficiency of these cells can be considerably improved by passivation of midgap states occurring at the semiconductor surface [6]. Conversely, introducing damages into the semiconductor surface like steps [7] or scratches [8] leads to an increased surface recombination velocity and hence to a reduction in the electrooptical performance of the junction.

It has been shown that a short photoelectrochemical etching (photoetching) of both p- and n-type semiconductors leads to a considerable increase in the photocurrent of various semiconductor junctions [9]. In addition to dislocations and defects which are preferentially removed from the semiconductor surface upon photoetching, a unique morphology of etch pits ($> 10^9$ $cm^{-2}$) is formed upon photoetching [9]. It has been clearly demonstrated [10, 11] that the distribution of the photoetch pits in CdTe shows no correlation with the dislocation distribution ($< 10^5$ $cm^{-2}$), as revealed by E-Ag reagent [12] and Nakagawa et al. etch [13]. This is probably true also for other photoetched semiconductors such as CdSe, CdS, ZnSe etc., since the density of photoetch pits is both too high ($> 10^9$ $m^{-2}$) and too uniform to be accounted for by dislocations or other gross material defects.

It has been proposed recently [14] that the morphology of photoetched surfaces is the manifestation of the dopant (non-stoichiometry) distribution close to the semiconductor surface. Strong evidence in support of that concept is the recent observation [10] that the etch-pits density and their size depend on the density of the localized charge carriers (dopant atoms, vacancies or interstitials) and the applied potential during photoetching.

Another test of that concept is that the surface density of the etch pits depends on the density of the charge carriers and not on their precise chemical nature. Formerly ZnSe which was chlorine doped exhibited a very similar etch pit distribution [9h] to that of photoetched Cd-chalcogenide semiconductors in which conductivity is achieved by introducing chalcogenide vacancies [9a, c].

## Experimental

In the present work we have employed two kinds of ZnS crystals. The white ZnS crystals (A electrode) were

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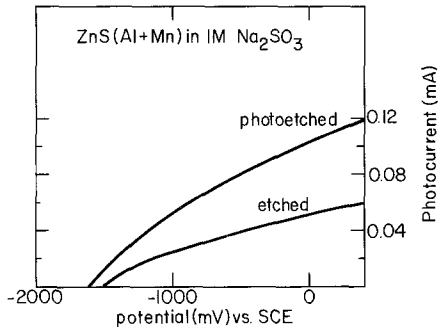
Fig. 1. I-V curves under illumination for Al doped ZnS (electrode A) prior and after photoetching
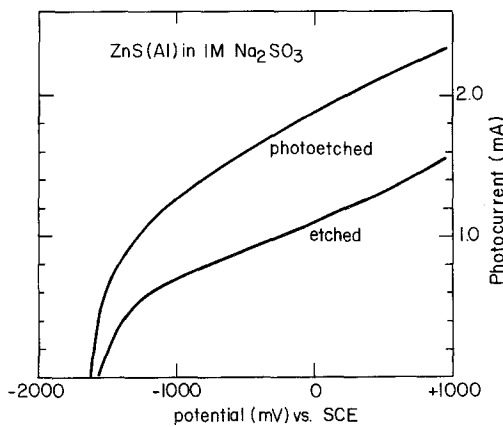


Fig. 2. I-V curves under illumination for Al+Mn doped Zn (electrode B) prior and after photoetching

Al-doped (100 ppm Al). The yellow ZnS crystals (B electrodes) were Al+Mn doped (0.01% Al; 1% Mn). They became conductive by annealing in Zn atmosphere at 800°C for 90 min. Prior to the preparation of the Ohmic contact the crystals were polished down to 0.3 µm and etched with a mixture of 3 parts concentrated $H_2SO_4$ and 7 parts saturated dichromate solution at 70°C for 5 min [4]. Other etching treatments had lesser effect. The same procedure was adopted also for the preparation of the front surface prior to each experiment. Ohmic contact was established by using a solid solution of 47% In, 48% Cd, and 4.7% Zn. This solid solution was amalgamated with a few mercury drops, and applied onto the back surface of the crystals and on one corner of the front surface. The crystal was then annealed at 450°C in oxygen free atmosphere and the quality of the Ohmic contact was checked by measuring the resistance across the crystal between the back and front surface. The I-V curves, in the dark and under illumination were measured in a conventional three-electrode electrochemical set-up with standard calomel electrode (SCE) as a reference electrode and a

large platinum mesh as a counter electrode. The solution for the I-V measurements was a transparent sodium sulfite (1M) solution. For the photoetching we have employed either the sulfite solution using reverse bias (+1V vs. SCE) and prolonged irradiation period or 4M perchloric acid, which necessitated a few seconds irradiation only. After photoetching the electrode was immersed in a polysulfide solution (2M with respect to $Na_2S$, S, and KOH) to dissolve elemental sulfur which was generated during the photoetching. The light source was a high pressure mercury lamp (absorption edge of ZnS 339 nm). The surface morphology of the crystals prior and after photoetching was determined by a scanning electron microscope (Jeol 35C).

## Results

Figures 1 and 2 show the I-V curves of A (ZnS+Al) and B (ZnS+Al+Mn) electrodes, respectively, under illumination, prior and after photoetching. The enhancement in the quantum efficiency of both electrodes after photoetching is clearly exhibited and is the result of preferential etching of defects and dislocations from the electrode surface. Consequently, the charge-transfer kinetics to the electrolyte is improved on the expense of surface recombination which decreases after photoetching. The surface of the electrode becomes somewhat opaque after that treatment. The reason for that opaqueness is revealed in Figs. 3 and 4 which show the SEM micrographs of A and B electrodes, respectively, before and after photoetching. The surface of photoetched ZnS exhibits a morphology that resembles the one observed with photoetched Cd-chalcogenides and ZnSe. The dense pattern of etch pits ($> 10^9$ cm$^{-2}$) is observed both in A and B electrodes. In addition to that, however, scratches, due mainly to the polishing, and dislocations are revealed by the photoetching process.

## Discussion

Several conclusions can be drawn from the present result: First and most important is that there exists a physical property common to all Cd- and Zn-chalcogenide semiconductors as a result of which a dense pattern of etch pits ($> 10^9$ cm$^{-2}$) is formed during photoetching. It seems that the exact chemical nature of the dopant, and the prior surface treatments are irrelevant here. Also important is the fact that photoetching leads to a removal of surface defects and dislocations which are not accessible to regular chemical etchants.
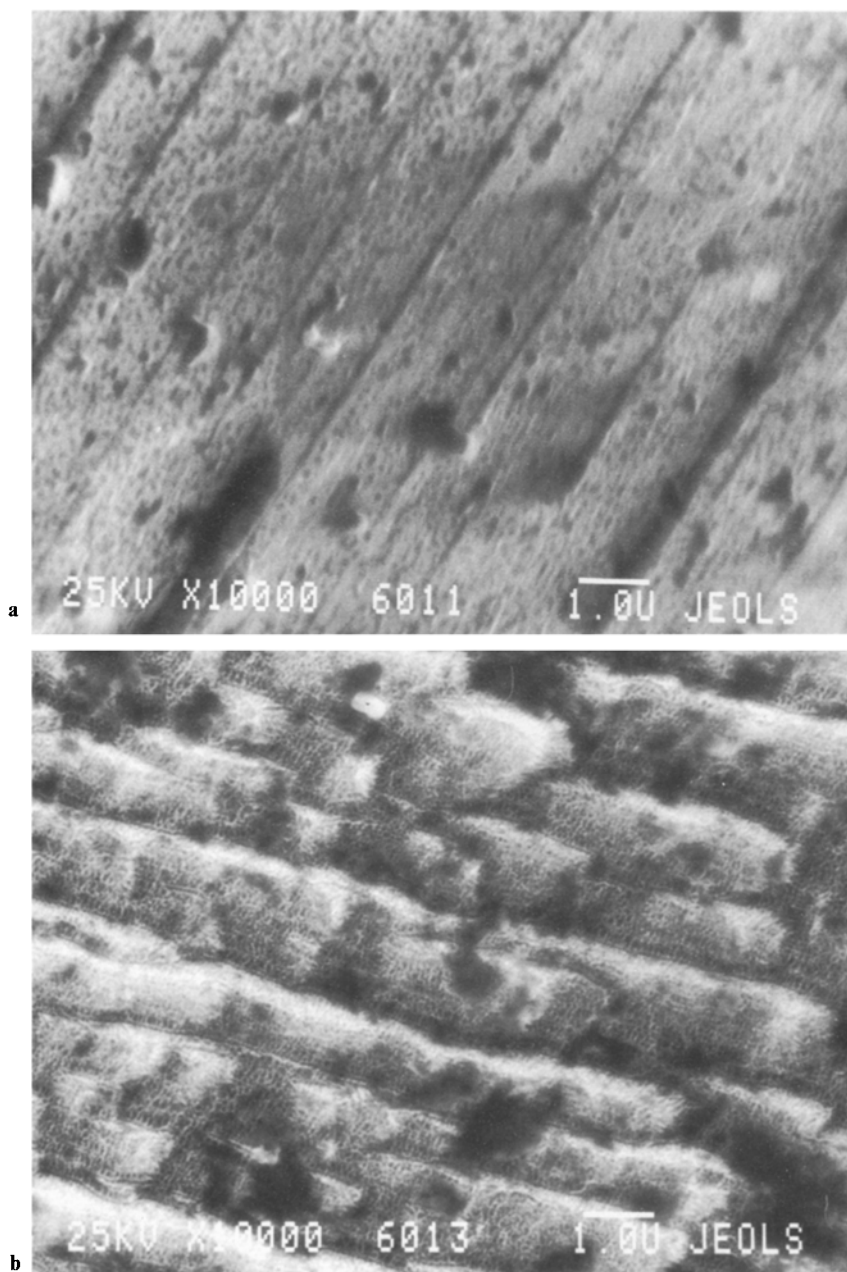
Fig. 3a and b. SEM micrograph of etched (a) and photoetched (b) ZnS (A electrode) (×10,000)

In trying to explain the possible connection between the localized charge carriers (dopants, vacancies or interstitials) and the generation of the etch pits two models were proposed [14]. The first one assumed that each localized charge carrier (dopant, nonstoichiometry) induces a local strain which makes it more sensitive to a chemical attack. The second theory assumes that the very existence of a Schottky barrier near the semiconductor surface implies that the localized charge carriers within the space charge layer are not neutralized by the electron charge. These localized charges induce microscopic electric fields which lead to the accumulation of photogenerated minority carriers at certain points on the semiconductor surface while the rest of the surface is relatively depleted of surface holes. Hence photoetching is non-uniform and hence the generation of the etch pit pattern.

Trying to assess the validity of each of the two approaches is a difficult task. However, most of the evidence is in support of the latter one. If the dopant atoms (nonstoichiometries) induce a local strain one may anticipate that a similar morphology would result from chemical etching and photoetching. On the other
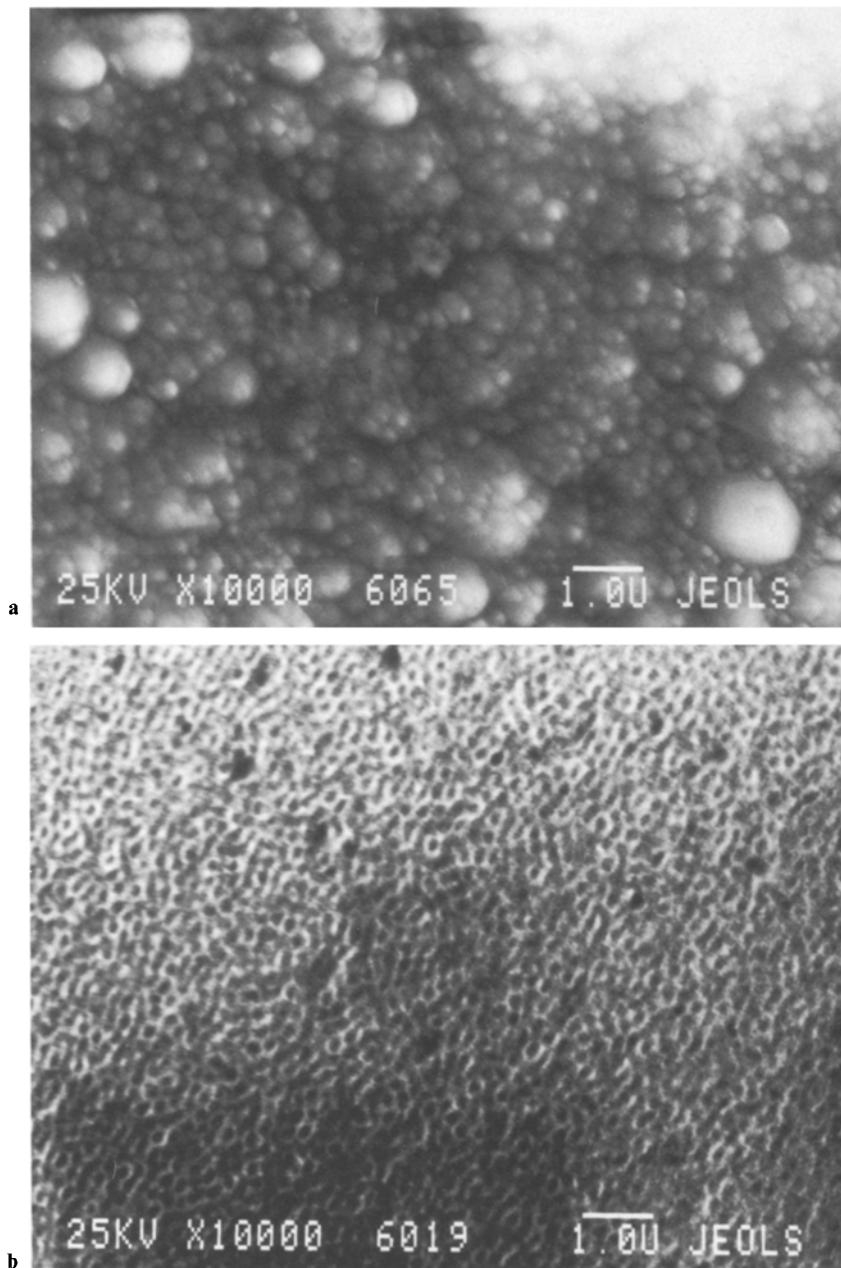
Fig. 4a and b. SEM micrograph of etched (a) and photoetched (b) ZnS (B electrode) ($\times 10,000$)

hand, suppose that the electric field within the space charge layer is non-uniform due to the ionized donors. Then the oxidizing species, which in the case of chemical etching come from the solution, are not expected to be influenced from that non-uniformity nearly the same as photogenerated holes which are generated within the space charge layer. For the same reason application of a forward bias during photoetching is expected to have much bigger impact on the surface morphology if its main effect is to reduce the nonuniformity of the electric field near the surface of the electrode. The fact that photoetching of various

CdSe, CdS, and ZnSe crystals which come from different sources (polycrystalline films are no exception) [9a, 14], and with different faces exposed to the solution, led to a similar morphology supports the hypothesis that non-uniformities in the electric field within the space charge layer are responsible for the generation of the unique morphology of photoetched surfaces.

Furthermore, the present results show that the exact chemical nature of the dopant atoms is also irrelevant in that respect, provided the two crystals show good conductivity, i.e. they incorporate localized charged

carriers (probably sulfur vacancies). Consequently, the present study supports the hypothesis that the morphology of photoetched surfaces is a manifestation of the non-uniformity in the electric fields within the space charge layer due to the presence of localized charge carriers in the crystal.

The implications of this theory are not limited to the photoetching process but are rather general for any semiconductor junction like Schottky barriers; $p - n$ junctions etc.

Further work is in progress which seems to support the hypothesis of non-uniform flow of charge carriers within the Schottky barriers and solid state junctions in general.

It is most likely that photoetching will have a positive effect on the performance of various electro-optical devices such as light emitting diodes and electroluminescing devices and work is in progress in our laboratory on that matter.

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