

Photostimulated gettering of deep band-gap impurities from semiconductors by resonance excitation: Fe from $\text{Cd}_{0.98}\text{Fe}_{0.02}\text{Se}$

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Impurities that lie deep in the band gap of a semiconductor (deep impurities) behave as a strong recombination center as shown by the Shockley-Read mechanism for surface recombination [A. Rothwarf and K. W. Boer, *Prog. Solid State Chem.* **10**, 71 (1975)]. Thus, removing such impurities from the semiconductor is imperative for the optimal operation of photonic devices and solar cells, in particular. In the following work a method is proposed to remove such impurities. In this process resonance excitation of electrons (holes) from the impurity level into the conduction (valence) band leads to ionization of the impurity, which in turn leads to fast outdiffusion of the impurity and its dissolution by a chemical (electrochemical) reaction at the semiconductor surface. As a demonstration of this principle Fe, which is a deep donor in CdSe, is selectively removed from a $\text{Cd}_{0.98}\text{Fe}_{0.02}\text{Se}$ crystal. A giant diffusion constant ($D = 10^{-9} \text{ cm}^2/\text{sec}$) is measured for Fe in this experiment. The application of this process for the control of impurity profiles in various semiconductor devices is briefly discussed.

Transition-metal impurities, which in many cases are present as deep levels in semiconductors, possess a permanent spin in their host lattice which lends itself to such applications as optomagnetic memory devices, detectors,^{1,2} etc. On the other hand, deep impurities, in general, lead to an efficient electron-hole recombination, which adversely affects the performance of photonic devices, and solar cells in particular. They also serve as strong scattering centers in electronic devices, which limit the mobility of majority carriers, and hence the performance of electronic circuitry. Being deep states, their valence state is not influenced by the position of the Fermi level, and consequently they do not influence the conductivity of the sample (if neutral), making it difficult to control their concentration in the host material. High-temperature zone refining methods are routinely employed to purify semiconductors from such impurities.³ However, such high-temperature treatments have various pitfalls, such as the diffusion of impurities from the walls of the crucible, loss of stoichiometry in compound semiconductors, etc. Gettering of oxygen and other impurities from semiconductor surfaces by surface damage³ and solid-state reaction with metal overlayers (see, e.g., Ref. 4) was shown to improve the performance of electronic and photonic devices. However, gettering of impurities from the semiconductor bulk is diffusion controlled and consequently requires high temperatures, in general.

In the present work, a room-temperature procedure to purify semiconductors from a well-characterized deep

(midgap) impurity is presented. The principle of operation of this method is explained by reference to the scheme presented in Fig. 1, using the particular case of Fe-doped CdSe. Iron is a substitutional deep donor in CdSe.⁵ Its neutral state (D^0) is situated some 1.15 eV below the bottom of the conduction band of CdSe.⁶ Excitation of iron atoms using a light source of $1.064 \mu\text{m}$

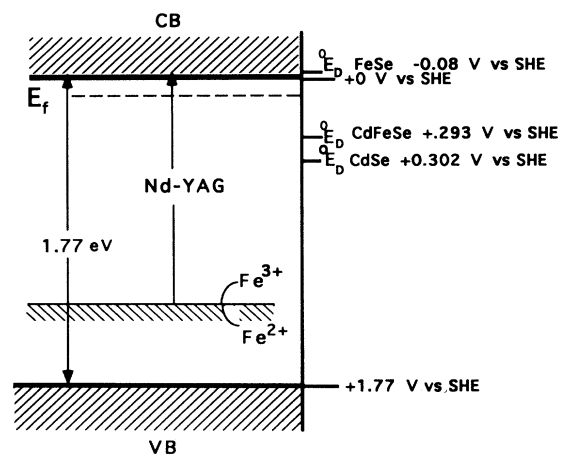


FIG. 1. Schematic representation of the resonance excitation photoelectrochemical etching method. Calculated decomposition reactions for a CFS crystal are given as well.

(1.15 eV) wavelength leads to injection of an electron from an iron atom into the conduction band of the host lattice, i.e., to a selective ionization of this impurity. This makes the ionized deep donor D^+ (Fe^{3+}) unstable with respect to its host lattice. If a thermodynamic driving force, such as (chemical and/or electrochemical) iron dissolution, or gas-phase reaction of the iron, is provided at the sample surface, a fast outdiffusion of the iron takes place from the bulk of the lattice. If supra-band-gap light is used, however, for the excitation, the entire lattice is excited and no selectivity with respect to the deep impurity occurs during photoetching. The latter process has been used in the past to remove shallow impurities and surface states in binary and ternary crystals, as well as in Si, which yielded high-efficiency photoelectrochemical cells.⁷⁻¹¹ Deep acceptors, such as V in GaAs,¹² can be removed by the present method, by selective excitation of a hole from the deep level into the valence band of the host material. Use of this technique for p -type materials is possible,¹³ although photocorrosion by surface electrons is more difficult to achieve.

Low-resistivity n -type $\text{Cd}_{0.98}\text{Fe}_{0.02}\text{Se}$ (CFS) crystals were grown by the Bridgman technique. The average concentration of Fe (2.3%) was determined by atomic absorption of the dissolved crystal and Rutherford backscattering analysis (2%). X-ray analysis and electron microprobe analysis (wavelength dispersive spectroscopy) confirmed that this material is homogeneous and constitutes a single phase for Fe concentration below 5%. The electrical properties of the crystals were determined by Hall measurements and are summarized in Table I. These results show that the crystal is n type with good electronic properties. Scanning electron microscopy (SEM) was performed with a Philips 515 scanning electron microscope. Transmission-electron microscopy in the imaging and electron diffraction modes were performed with a Philips CM12 microscope. (1120)-oriented crystals were cut, polished, and chemically etched by a Aqua-Regia (1:3) HNO_3 :HCl mixture. Attempts to use another etchant did not yield superior results. The crystals were subsequently immersed in a concentrated polysulfide solution (to remove elemental Se and oxides thereof), 10% KCN (to remove polysulfide ions left from the previous treatment), and finally in concentrated HCl (to remove iron oxide). X-ray photoelectron spectroscopy (XPS) indicated that this kind of treatment leads to a stoichiometric surface having 2% (sensitivity of ca. 0.2%) iron. Resonance excitation photoelectrochemical etching (REPE) was performed using a Nd:YAG (yttrium aluminum garnet) laser (1.064 μm wavelength) of intensity 1.2 W/cm^2 . No heating of the

sample during the treatment could be observed. This is understandable in view of the relatively weak absorption of the light at this wavelength. For the photoetching (PE) with supra-band-gap excitation and for the I - V measurements in polysulfide solution, a tungsten halogen lamp (200 mW/cm^2) replaced the laser light. A conventional three-electrode electrochemical setup was used for the REPE with Pt mesh as a counter electrode and Pt tip as a reference electrode. Reverse (anodic) bias of 0.9 V versus Pt was used for this process. The photocurrent increased from 1 to 38 mA/cm^2 during the first 100 sec of REPE and then it leveled off (25% HCl). If only 10% HCl was used the photocurrent increased first very rapidly and leveled off at 20 mA/cm^2 after 20 sec, due likely to the hydrolysis of the Fe^{3+} which passivated the sample surface. This was confirmed by measuring the solubility of Fe_2O_3 in different concentrations of HCl. Below 25% the solubility of the oxide was not complete. Photoluminescence was measured with a standard setup.

Figure 2 shows the results of the XPS analysis for CFS crystal after various surface treatments. The spectra were normalized to equal intensity of Cd (arb. units = 100). The reference data [Fig. 2(a)], which is typical of a

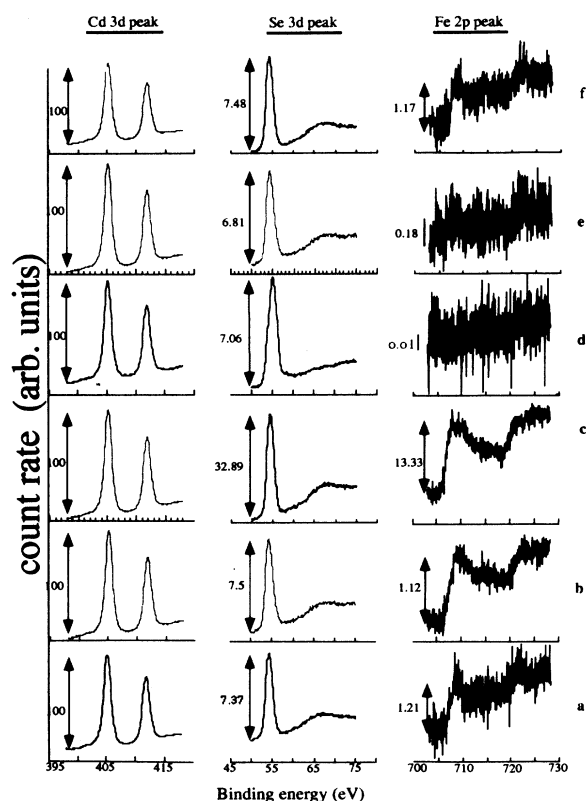


FIG. 2. XPS data for the CFS crystal which was treated in different ways. (a) Reference. (b) Photoetched with white light in 10% HCl, chemically cleaned, 15-Å sputtered. (c) Photoetched with a Nd-YAG laser in 10% HCl, no chemical cleaning, no sputtering. (d) Photoetched with a Nd-YAG laser in 10% HCl, chemically cleaned, no sputtering. (e) As in (d) but 15-Å sputtering. (f) As in (d) but sputtered 1400 Å.

TABLE I. Results of Hall effect and resistivity used for the determination of the electronic properties of the $\text{Cd}_{0.977}\text{Fe}_{0.023}\text{Se}$ crystal.

Sample	Density of free carriers (N_d) (cm^{-3})	Specific resistivity (ρ) ($\Omega \text{ cm}$)	Electron mobility (μ) ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
$\text{Cd}_{0.977}\text{Fe}_{0.023}\text{Se}$	1.3×10^{16}	1.5	300

stoichiometric surface, was obtained with a cleaved or chemically etched crystal after a few Å of its surface were stripped off by Ar-ion sputtering (to remove carbon contamination). When above-band-gap light is used for the photoetching [Fig. 2(b)], no appreciable deviation from the CFS stoichiometry is observed after chemical cleaning and, hence, no selectivity with respect to iron exists. In Fig. 2(c) are shown the spectra of a CFS crystal which was treated by REPE, in 10% HCl (20 sec), and not cleaned afterwards. In this case, a substantial excess of both Se and Fe are observed. Furthermore, the line shape of the $2p$ spectrum of iron suggests that both Fe^{2+} (709.7 eV) and Fe^{3+} (711.2 eV) exist at the surface in the ratio close to 1:1. Oxygen is present in substantial quantities in this sample. The surface of PE (not cleaned) CdSe, on the other hand, exhibits little oxygen peak, in general. It can be concluded, therefore, that the large concentration of outdiffusing iron at the surface led to partial hydrolysis and precipitation of some iron. The next studied surface [Fig. 2(d)] is a CFS crystal which was REPE for some 20 sec only (to enable us to examine the CFS/CdSe interface) and subsequently cleaned by the chemical procedure outlined above. Here, a pure and stoichiometric CdSe is observed on the virgin surface, i.e., iron has been completely removed from a surface layer of the CFS crystal. Only after ca. 1400-Å sputtering [Fig. 2(f)], is the original CFS composition reestablished. An XPS analysis of REPE-treated (25% HCl; 100 sec) CFS crystal shows that a substantial depletion of iron is observed even at depths larger than $3\ \mu\text{m}$. However, in this case, some precipitation of iron oxide (most likely Fe_3O_4) is observed, which is not easily dissolved. This analysis suggests a fast outdiffusion of iron during REPE followed by its dissolution and chemical oxidation of selenium at the semiconductor surface.

The diffusion coefficient of substitutional impurities in semiconductors, at temperatures of a few hundred degrees Celsius, is rather low, i.e. $< 10^{-15}\ \text{cm}^2/\text{sec}$.^{14,15} Very high diffusion coefficients ($1.5 \times 10^{-11}\ \text{cm}^2/\text{sec}$ at 600°C) were reported for Zn (substitutional impurity) in GaAs.¹⁶ On the other hand, small ions which have an appreciable density of interstitials, such as Li^+ (ionic radius $0.61\ \text{Å}$), exhibit large diffusion constants (ca. $10^{-10}\ \text{cm}^2/\text{sec}$) at such temperatures. In the present process, iron, which is a substitutional impurity, was removed by REPE from a layer larger than $3\ \mu\text{m}$ at about 100 sec. Thus, a giant diffusion constant of approximately $10^{-9}\ \text{cm}^2/\text{sec}$ for Fe in CdSe can be estimated for the present experiment at room temperature. A plausible explanation for the fast diffusion is that Fe^{3+} , which is generated by the resonance excitation, is unstable in the substitutional site and due to its small size ($0.64\ \text{Å}$) it can accommodate a neighboring interstitial site. Once in the interstitial site it recombines with an electron from the Fermi sea, and becomes Fe^{2+} . This species, being unstable in its interstitial position, kicks out a neighboring substitutional Fe^{2+} to an interstitial site, or enters into an empty Fe_v site thus triggering a fast chain process. Fast diffusion of Cd in CdS (Ref. 17) and Se in CdSe,¹⁸ at elevated temperatures, was interpreted¹⁸ by the abundance of Cd and Se interstitials in the respective lattices. A mechanism for

the enhanced migration of interstitial impurities through various charged states was proposed.¹⁹ This mechanism involves a coupling of the potential diagram of the neutral ground state, which is most stable in the interstitial tetrahedral site, with that of the charged state ($+1$), for which the saddle point between two lattice atoms (hexagonal site) is the most stable point. Since the two diagrams have different stable points in space, fast diffusion of the impurity by excitation hopping, and relaxation is expected. Theoretical calculations provided evidence that a similar mechanism is responsible for the disappearance of interstitial Si from irradiated Si at low temperatures.²⁰ A similar mechanism could lead to an enhanced diffusion of the Fe(II) substitutional impurity in the present case. A recent report showed that hydrogen diffusion is enhanced in $\alpha\text{-Si:H}$ (hydrogenated amorphous silicon) by intense illumination with above-band-gap energy.²¹ Since no resonance excitation of the impurity is provided in this experiment, the diffusion constant increases by only about one order of magnitude, compared with the unilluminated sample.

The influence of the space-charge field on the REPE process has not been investigated as yet. If the rate-limiting step of the process is the dissolution of the Fe ions at the interface, then diffusion of iron ions against concentration gradients is expected to be slow. In that case, the drift of the Fe^{3+} ions is expected to be enhanced by the space-charge field near the semiconductor surface.

Transmission-electron microscopy shows that the REPE processed material is porous, yet its crystallinity is preserved, as shown by the electron-diffraction image. The lattice constant of the unit cell agrees with that of pure CdSe ($c = 7.01\ \text{Å}$; $a = 4.29\ \text{Å}$).²² Using SEM, it was found that the porosity of the material after REPE is substantially smaller (10^8 etchpits/ cm^2) than that of the CFS (or CdSe) crystal after PE with above band-gap light (10^{10} etchpits/ cm^2).

The procedure also has a remarkable influence on the photovoltaic response of the material, as shown, for example, in Fig. 3. The chemically etched crystal, as well as the cleaved crystal, exhibits poor photocurrent (curve 1). PE, using the above-band-gap excitation, leads to a threefold to fivefold increase in the photocurrent and an appreciable increase in the photovoltage (curve 2). The favorable influence of PE on the photovoltaic properties of CdSe are well documented,⁹ and were attributed to the cleaning of the surface from recombination centers associated with shallow (near-band-gap) impurities. However, by far the highest photocurrent is obtained after REPE (curve 3). Photocurrents of $17\ \text{mA}/\text{cm}^2$, under $200\ \text{mW}/\text{cm}^2$ illumination, typical of a pure CdSe electrode, were obtained, representing a spectrally averaged quantum efficiency of ca. 70% (saturation photocurrents of up to $20\ \text{mA}/\text{cm}^2$ were obtained under a reverse bias of $200\ \text{mV}$). The slight decrease in the photovoltage, following REPE, is due to the fact that we have attempted to optimize the photocurrent, rather than the power efficiency, and thus continued the process far too long (ca. 2 min).⁹ The evolution of the spectral response due to the different surface treatments is shown in the inset of Fig. 3. The spectral response of the REPE sample exhib-

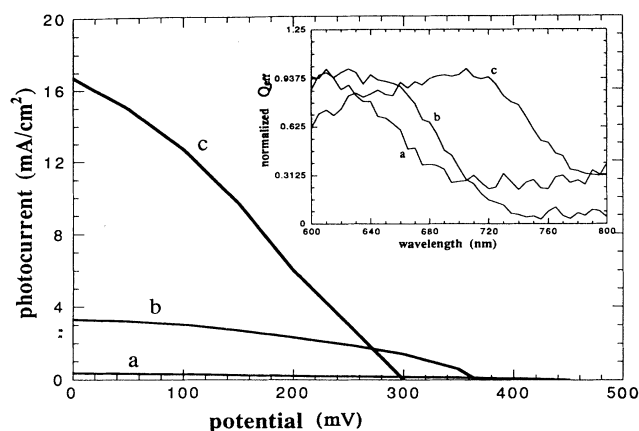


FIG. 3. I - V curves of a CFS crystal in a polysulfide electrolyte (2M with respect to each S^{2-} , S, and KOH). Illumination was provided by a calibrated tungsten-halogen lamp (200 mW/cm^2). Curve *a*, chemically etched surface. Curve *b*, photoetched by above-band-gap light. Curve *c*, after resonance excitation photoelectrochemical etching. Inset: normalized spectral response of the same samples in the same electrolyte (normalization factors are 62,22,1.25 for curves *a*, *b*, *c*, respectively).

its a 48-fold increase, compared with the chemically etched crystal. The band gap of the CFS crystal before REPE, which is obtained from the Gärtner-Butler analysis,²³ is 1.77 eV, which is 50–60 meV higher than that of a pure CdSe crystal. After REPE, an appreciable redshift is observed in the spectral response, which is consistent with the transformation of the CFS crystal into a pure CdSe, at the semiconductor surface. However, the calculated band gap of the CFS crystal after REPE (1.60 eV) is even lower than the band gap of pure CdSe (1.72 eV). This fact is indicative of a photocurrent which results from internal excitation of photoelectrons (from the Fe d level to the conduction band). Since Fe is absent at the semiconductor surface, the collection of photoelectrons of energy $< 1.72 \text{ eV}$ is due likely to a new junction formed at the interface between the CFS and the CdSe (designated d - n junction) beneath the original semiconductor-polysulfide electrolyte junction. This excitation can also explain the degradation of the photocurrent with time. In contrast with the band-to-band excitation of CdSe, for which stable photocurrents over prolonged periods of time have been demonstrated in polysulfide electrolyte, the internal transition in CFS may lead to fast-iron migration (similar to the REPE process) and precipitation of a blocking FeS film at the semiconductor-electrolyte interface, and hence to a degradation of the photocurrent.

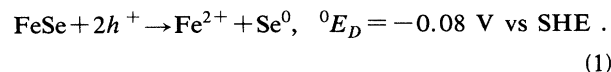
There is no direct information on the doping level, carrier lifetime, etc., of the porous material which is formed by REPE of the CFS crystal. Numerous measurements show that the effective doping density of (porous) CdSe, after photoetching with above-band-gap light, decreases.²⁴ It was attributed to the cleaning of the sample from recombination centers, associated with shallow donor impurities, near the semiconductor surface.²⁴ The mechanism proposed for the REPE process is not indica-

tive of any preferential affinity of the process towards shallow donor states, and hence we do not expect this process to lead to substantial changes in the doping density of the materials.

The small redshift of the spectral response, observed after white-light PE (10 meV), which was observed before for other semiconductors, was also attributed to the cleaning of the sample from recombination centers, associated with shallow donor impurities, near the semiconductor surface.²⁴

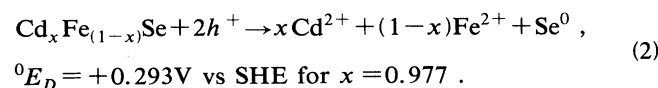
Photoluminescence measurements²⁵ show that the band gap of the CFS crystal is 60 meV higher than that of CdSe (e.g., 1.855 eV for CFS compared with 1.795 eV for CdSe at 75 K), thus confirming the findings of the spectral response.

Ideally, the chemical reaction of the REPE process should involve the outdiffusion of the iron from the lattice and selective decomposition of the FeSe at the semiconductor surface alone, i.e., in our case,

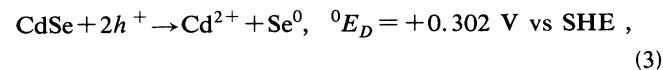


Here, SHE is standard hydrogen electrode and 0E_D is the decomposition potential calculated from thermodynamic tables.²⁶

For a totally nonspecific corrosion (i.e., for chemical etching and PE with above-band-gap light) the chemical reaction is,²⁷



In practice, the corrosion reaction in REPE experiments is not specific enough [i.e., not only reaction (1) occurs] so that partial decomposition of the CdSe cannot be avoided altogether according to the following reaction:



which leads to a dissolution of cadmium ions and an excess of elemental selenium at the surface of REPE treated CFS crystal. This result, however, had no ramification on the high photoresponse of the semiconductor after REPE, as shown in Fig. 3, because the excess selenium which is produced by reactions (1) [and (3)] is removed by the procedure of chemical cleaning, which follows REPE, and consequently a stoichiometric CdSe layer is obtained [see Fig. 2(d)]. Future experiments will try to achieve a better selectivity of reaction (1). One way to do that is to excite the impurity to its (first) excited state, using one wavelength, and subsequently to ionize the excited state using another wavelength. In this manner, no excitation of the host lattice will occur and its photocorrosion will be avoided altogether. Thus Fe in the CFS lattice can be first excited to its 5T_2 state using 0.37-eV light,²⁸ and further ionized by 0.75-eV light. The decomposition potential of the CFS crystal and the two binary compounds (CdSe, FeSe) are found to be more negative than the valence-band edge, and the Fe level ($E_v \pm 0.64 \text{ eV}$), which renders the material unstable against photoanodic decom-

position.²⁶ These values suggest another means to achieve a better selectivity for the dissolution of Fe through the control of the bias during REPE. If the bias is controlled so that the decomposition potential of FeSe is above the Fe level, and that of CdSe is below it, selective decomposition of the FeSe will occur. The position of the band edges (during REPE) was estimated from the open circuit potential under strong illumination and it agrees with published values for CdSe.²⁹

In summary, therefore, we have suggested a new

method for chemical cleaning of semiconductors from midgap impurities at room temperature, and demonstrated selective removal of Fe from an Fe-doped CdSe crystal. Numerous applications can be thought of for this method.

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