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Photoelectrochemical Study of n-InP: Redox Processes Using Electroluminescence as Mechanistic Probe

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Electroluminescence (EL) due to band-band transition was observed for n-InP single crystal electrodes in solutions containing current doubling reagents like peroxodisulfate and various redox electrolytes. The mechanism for the EL emission in relation to surface properties of n-InP crystals in these electrolytes is presented. The cathodic decomposition process of n-InP electrodes involved in various electrolytes especially in peroxodisulfate medium has been analyzed from the EL emission as a function of electrode potential under steady state as well as pulsed conditions. The intensity of the EL signal depends on the electron density at the interface which is controlled by the potential and on the chemical composition of the electrode surface. Moreover, a hydrogen evolution reaction reduces the EL efficiency at higher cathodic potentials. Though the potential has no effect on the shape of the EL spectra, a significant change in EL intesity was observed. In all the electrolytes used the InP electrodes seem to decompose during cathodic polarization to form indium metal. The change in the surface composition plays an important role in the relation between potential and the EL intensity. Moreover, during pulsed polarization the EL behavior is different from the steady state conditions and also depends on the concentration of the electrolyte species.

The Electroluminescence (EL) measurement has been a useful technique for the understanding of electrochemical reaction mechanism at semiconductor/electrolyte junction.[1–11] Presently, we discuss the EL study as a probe to understand the surface properties of semiconductors. EL is usually caused by minority carrier injection under forward bias condition. For example in the case of an n-type semiconductor biased cathodically, hole injection from the electrolyte species to the valence band is possible.

Basically, EL emission is induced by two types of solution species at the semiconductor/electrolyte interface caused by current doubling or normal redox species. The one using a current doubling reagent (2 electron transfer) involves both conduction and valence bands and the other by a normal redox electrolyte (1 electron transfer) involves mainly the valence band of the semiconductor. In these processes, band gap emission should be observed in the absence of lattice defects and bulk impurities. Moreover, in the presence of surface states the relaxation pathways are increased. Most of the reported EL spectra show transitions involving surface states, lattice defects, or impurity states.[2–5,8–10,11–14,25]

Indium phosphide (InP) has been one of the few technologically advanced materials (III-VI) and its luminescent properties at p-type/n-type semiconductor, semiconductor/metal, or liquid junctions have become well known. It has been reported in earlier publications[11,25] that the InP/aqueous acid interface consists of a chemically passive thin layer of In_2O_3 which reduces the surface recombination of carriers at the above interface in electrochemical solar cells. In general, the process of hole injection from the redox electrolytes into small band gap semiconductors is usually associated with that of corrosion.[15–17] Moreover, in the case of InP, the chemistry of the interfacial oxide films which act to give the material its decisive advantages is not yet clear.

In this work, we examined the electrochemical as well as electroluminescent properties of single crystal n-InP electrodes using current doubling reagents like peroxodisulfate and various redox electrolytes. EL initiated by hole injection from redox/current doubling reagents in solution was studied under both steady state and pulsed potential conditions. This study provides more details about the semiconductor stability which basically depends on the surface properties of the semiconductor crystal. Since InP is known for its cathodic decomposition which leads to an entirely different surface morphology, it is interesting to probe the surface properties by the EL observation under various conditions. The factors which are important in determining whether a redox process can really compete with the cathodic dissolution and the hydrogen evolution at n-InP in order to produce efficient EL as well as the semiconductor surface stability are also described.

Experimental

Materials: n-InP (orientation: 100, dopant: Sn, donor density: 1.0×10^{18} cm^{-3}, resistivity: 3.1×10^{-3} Ω cm, mobility: 2.0×10^{3} cm^{2} V^{-1} sec^{-1}) crystals obtained from Nippon Minning Ltd., were used in the present study. All the chemicals used were of AR grade and the electrolyte solutions were prepared ultrasonically with distilled water.

Electrochemical Measurements: A simple Pyrex cell with a single compartment was used for all the experiments. Electrodes were made in the usual way by making ohmic contacts to the crystals with Ga-In eutectic. The procedure for mounting the crystals on the glass holders is shown elsewhere.[23,24] Br–methanol solution was used to etch the electrodes. The potential of the electrode was controlled by a

PAR 173/PAR 175 potentiostat-galvanostat/programmer system with respect to a saturated calomel electrode. A Pt wire was used as the counter electrode.

Electroluminescence Measurements: The EL spectra were mainly obtained with a spectrofluorometer (Fluorolog). The sample position of the spectrometer was modified to take our cell. The detection system had a good response in the range from 400—950 nm. The EL spectra were corrected separately for the system response especially in the IR region (800—950 nm). For pulsing experiments the electrode was pulsed between 0.0 V vs. SCE and a given negative potential. The whole system was controlled by a computer provided with the spectrofluorometer system. Here, the EL signals were detected by a photomultiplier which is connected to a high voltage power supply and displayed in the computer. The spectral data obtained were stored on a floppy disk.

Results

Hole Transfer during Redox Process at InP: Figure 1 shows the band energy scheme of InP with the occupied and the unoccupied states of peroxodisulfate redox species. According to this it is possible for both the bands of the semiconductor to involve in the charge transfer process and thereby a photocurrent doubling phenomenon is also expected. This is found to be possible at a p-InP electrode under illumination. Figure 2 shows the *i–v* characteristics of p-InP photoelectrode in acid medium before and after the addition of peroxodisulfate during irradiation. Here, we find that the current doubling effect takes place with about 50% increase in the photocurrent when peroxodisulfate is added.[23,24] On the other hand, reduction of peroxodisulfate ions occur at n-InP in dark at higher cathodic potentials than for illuminated p-InP electrodes. The current–voltage (*i–v*) curves for n-InP electrode in 0.5M H_2SO_4 (1 M=mol dm^{-3}) and with the addition of peroxodisulfate ions are shown in Fig. 3. From the observation of cathodic currents at n-InP (in dark) and p-InP (in light)/peroxodisulfate in an aqueous medium, it is clear that the holes are injected into the valence band of the semiconductor. This indicates the reduction of peroxodisulfate ions at n-InP (in dark) causes injection of holes into the valence band. Moreover, this reduction yields higher cathodic currents than that of H^+/H_2 which occurs at more cathodic potentials. This result implies that with n-InP electrodes the rate determining step may not be determined by the charge carriers within the electrode, but possibly determined by the charge transfer of the redox system. The normal redox electrolytes used were $K_3Fe(CN)_6$, $Ce(SO_4)_2$, and

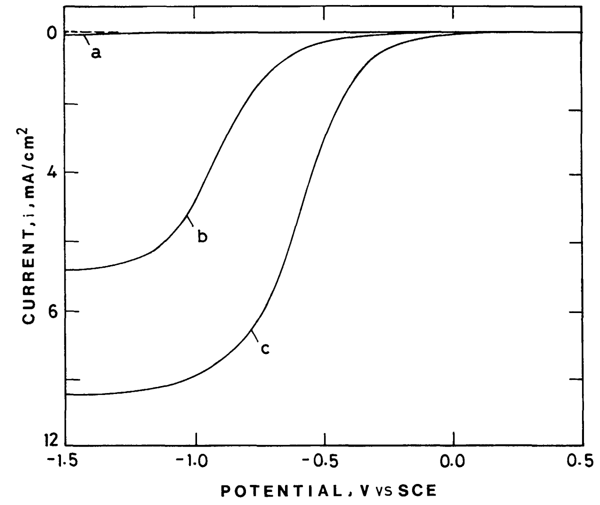

Fig. 2. Current-potential curves for p-InP in (a) 0.5 M H_2SO_4 (in dark); (b) 0.5 M H_2SO_4 (under illumination); (c) 0.5 M H_2SO_4+0.1 M $Na_2S_2O_8$ (under illumination).

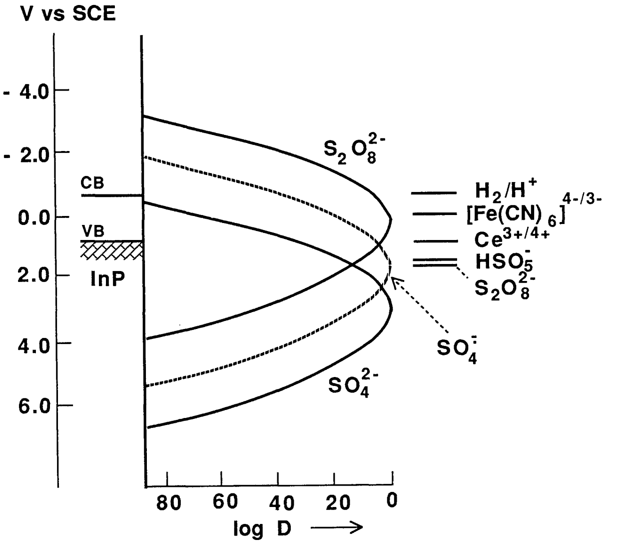

Fig. 1. Energy scheme for n-InP/distribution of energy states of peroxodisulfate at the interface together with the energy levels of other redox species.

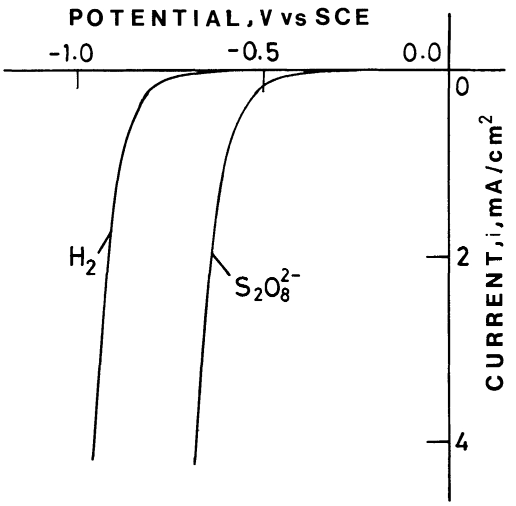

Fig. 3. Current-potential relationship of an n-InP single crystal electrode in 0.5 M H_2SO_4+0.1 M $Na_2S_2O_8$.

peroxomonosulfate (OXONE) and all of them were found to inject holes into the valence band at higher cathodic polarization to produce EL. The redox energy levels for these electrolytes are also indicated in Fig. 1. The distribution function of the occupied states for a redox system is given as,[40]

$$D_{\mathrm{red}} = \exp\left[-\frac{(E - E_{\mathrm{f}} + \lambda)^2}{4kT\lambda}\right] \tag{1}$$

Where E_{f} is the Fermi level of the redox system which is equivalent to the redox potential, E is the bias potential and λ is the rearrangement energy. The energy distribution curves of the peroxodisulfate species shown in Fig. 1 has been calculated using the above equation with a λ value of 1.4 V as given in Ref. 28.

Effects of Potential on the EL Spectral Distribution and Intensity: Figure 4 presents the EL spectra of n-InP electrode obtained by pulsing between 0.0 V vs. SCE and a cathodic limit in peroxodisulfate electrolyte. The EL has almost the same spectrum as that of photoluminescence (PL) in air. Emission rises around 823 nm (1.5 eV) and shows a maximum at 893 nm (1.39 eV) while the band gap seems to lie around 915 nm (1.36 eV). This is the band edge emission which seems to be efficient and no sub band emission is detected with the present photomultiplier used. In the same figure significant changes in EL intensity have been observed with changes in the cathodic potential limit, whereas there is no shift in spectral distribution. This could be understood more clearly by normalizing curve 'a' and 'e' of Fig. 4 to the same peak height.

EL and Current Characteristics during Steady State Polarization: EL and current were measured for n-InP electrodes in various redox electrolytes as mentioned above. In all cases, high cathodic current flows when the potential is negative of V_{fb} (−0.7 V vs. SCE, estimated from Mott–Schottky plot) as well as positive of V_{fb} and it increases with potential. Since the cathodic decomposition of the InP surface is a typical process the EL intensity decreases at potentials negative of −1.0 V vs. SCE. Moreover, the reverse anodic polarization does not reproduce this peak in almost all the redox electrolytes used. For the sake of simplicity we discuss the EL characteristics mainly in acidic medium containing peroxodisulfate ions.

Figure 5 shows the EL and current behavior of n-InP with potential in 0.5 M H_2SO_4 containing 1 M peroxodisulfate ions. EL rises around −0.7 V vs. SCE and reaches a maximum at −1.0 V vs. SCE and decreases with further polarization whereas the current increases. This EL peak is irreversible during the potential sweep in the anodic direction but appears again during repeated cathodic scans i.e., the EL curve is reproducible only when the electrode is polarized back to 0.0 V vs. SCE. This suggests that under steady state polarization the surface composition of InP changes at higher cathodic polarization even in the presence of strong current doubling redox species. The high current density observed here indicates the electrolyte reduction proceeds also without hole injection. This is explained as low current yield of electroluminescence.[11]

Effects of Pulsed Potential on EL Intensity in Various Redox Electrolytes: In pulsed experiments the electrodes were pulsed mainly between 0.0 V

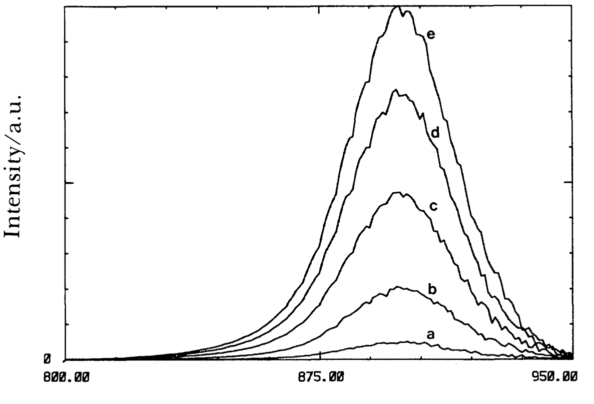

Fig. 4. Potential dependence of emission spectrum vs. EL intensity of n-InP in acid medium containing 1 M $Na_2S_2O_8$. The electrode was pulsed between 0 and a) −0.7; b) −0.75; c) −0.8; d) −0.85; e) −0.9 V vs. SCE at 167 Hz.

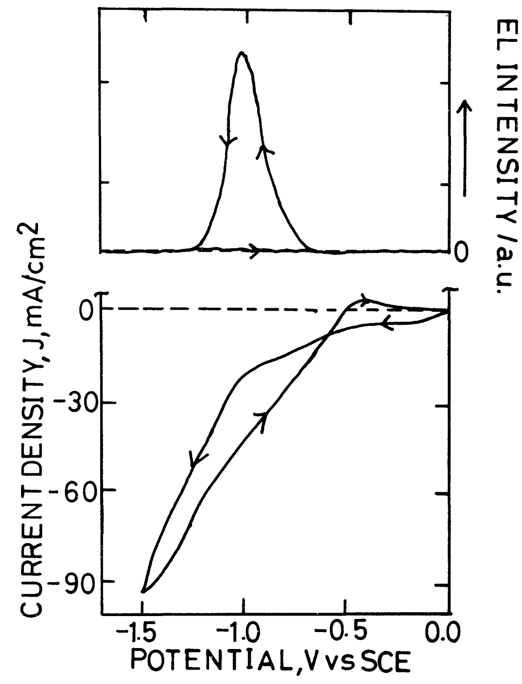

Fig. 5. EL intensity (top) and current (bottom) vs. potential of an n-InP electrode in 0.5 M H_2SO_4 and 1 M $Na_2S_2O_8$. Scan rate, 20 mV sec^{-1}.

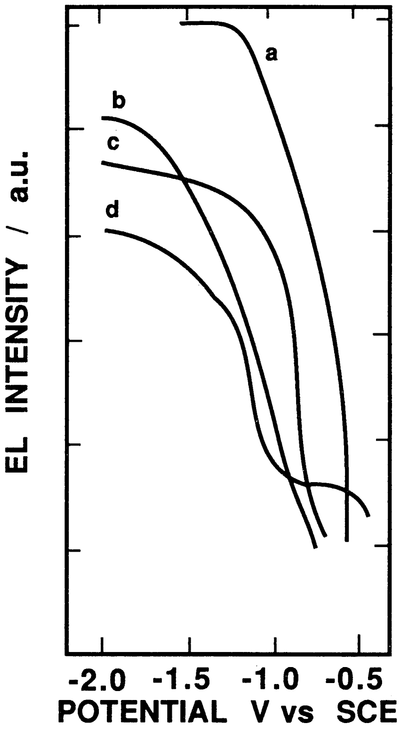

Fig. 6. EL intensity vs. pulsed polarization of n-InP electrode in a) 0.5 M H_2SO_4+0.1 M $Na_2S_2O_8$; b) 0.1 M HSO_5; c) 0.5 M H_2SO_4+0.1 M $K_3Fe(CN)_6$; d) 0.5 M H_2SO_4+$Ce(SO_4)_2$. Pulsing frequency is 167 Hz.

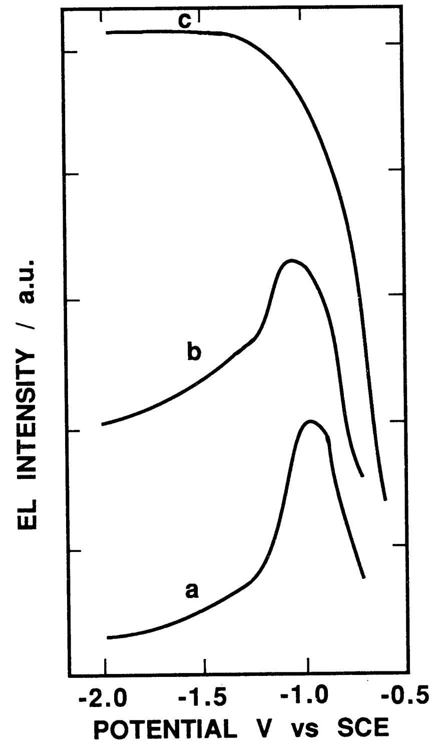

Fig. 7. EL intensity vs. pulsed polarization of n-InP electrode in 0.5 M H_2SO_4 and different concentrations of $Na_2S_2O_8$. a) 2×10^{-3} M; b) 2×10^{-2} M; c) 1 M. Pulsing frequency is 167 Hz.

(5 ms)-cathodic limit (1 ms). Pulsed potential dependence of EL intensity of n-InP electrodes in various electrolytes are shown in Fig. 6. The EL intensity increases with the increase in the cathodic potential limit in all the electrolyte media used. The current behavior also seems to be of similar trend. EL intensity is found to be higher for current doubling reagents like peroxodisulfate than that for normal redox electrolytes. Unlike the behavior in steady state experiments, the EL intensity increases with increase in cathodic potential limit. Moreover, when the concentration is low (2×10^{-2} M) the EL behavior during pulse potential is similar to steady state condition. Figure 7 shows the EL intensity vs. concentration of peroxodisulfate in acid medium. Here, the increase in the peroxodisulfate ionic concentration enhances the EL intensity, but at low concentrations the behavior is similar to that of steady state condition.

Discussion

As discussed before, emission at semiconductor/electrolyte interface is made possible by hole injection.[2,22)] We have investigated this at n-InP/electrolyte junction by two ways using I). current doubling reagent (2 electron transfer) II). normal redox electrolytes (1 electron transfer). Effective emission takes place in both cases a). when the energy level corresponding to the radical species produced in I and the redox level of II lie positive enough to inject holes into the valence band b.) the cathodic bias should be adequate to cause drifting of electrons towards the interface. The mechanism of EL occurring in these two processes are explained as below:

It is well known that n-type semiconductors under cathodic polarization in solutions containing a current doubling reagent like peroxodisulfate produce EL,[28)] here, $S_2O_8^{2-}$ is reduced by electrons of the conduction band producing a highly unstable radical $SO_4^{\overline{\cdot}}$ which is a strong oxidant having a very positive potential and capable of injecting holes into the valence band. Significant EL intensity is only detected at potentials near to or negative of V_{fb} (weak cathodic bias) where double injection occurs (Fig 8a). In the case of a normal redox electrolyte an electron transfer from the valence band to the unoccupied states of the redox species is possible when the cathodic bias potential is high enough (strong cathodic bias) where a strong accumulation layer forms at the interface and holes can be injected into the valence band (Fig. 8b).

Moreover, these recombination processes proceed either directly or indirectly via surface states, bulk defect or an impurity center. There are a lot of studies on the sub-band gap emission involving surface states[2,8,18,25,27)] and due to bulk impurities.[4,13,14)] Presently, we have observed the emission band of n-InP crystal having maximum at 893 nm (1.39 eV) which

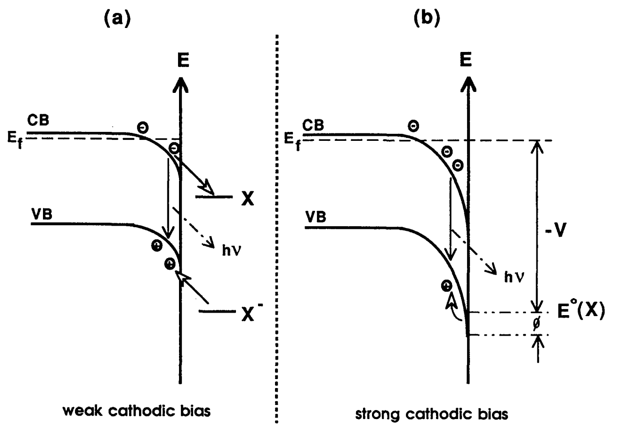

Fig. 8. Band bending and hole injection at the interface between n-InP and a) current doubling species, b) normal redox species. (Where −V is the additional bias needed for hole injection).

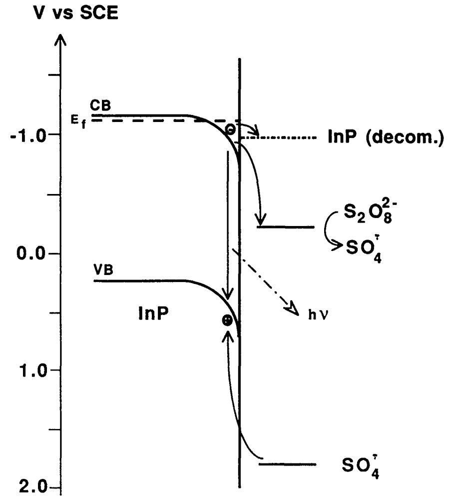

Fig. 9. Mechanism of hole injection, cathodic dissolution, and electroluminescence of n-InP in peroxodisulfate electrolyte. (pH=1).

corresponds to the band gap energy (1.36 eV). In general, surface states as well as lattice defects cause sub band emission. As mentioned before, the energy of the peak in the EL spectra of InP used in this study agrees well with energy gap, suggesting that the band-band transition is the dominating process in the generation of EL. Previous report by Heller et al., also shows similar band gap transition which is observed by hole injection mechanism in nitric acid. Observation of no sub band gap emission in the present study can be explained as a). low surface recombination velocity at air exposed n-InP surfaces[29] b). the presence of a thin, hydrated layer of In_2O_3. This layer is effective in reducing the rate of non-radiative recombination in InP based photoelectrochemical cells.[30–33]

Observation of luminescence at n-InP during peroxodisulfate reduction at cathodic polarization indicates the two electron transfer process with peroxodisulfate involving both bands of the semiconductor and confirms the hole injection process. At potentials approaching flatband potential, conduction band electrons and injected holes are no longer spatially separated and can therefore recombine either through states within the band gap, or directly causing EL. Though there is significant current flow till −0.7 V vs. SCE no EL is observed, showing that electrolyte reduction proceeds also without hole injection which is also referred as the low current yield of electroluminescence. At sufficiently cathodic potentials the semiconductor dissolution is expected to be prevented in the presence of current doubling reagents like peroxodisulfate. But, the decrease in EL after a certain potential (Fig. 5) indicates the typical surface change of InP even in the presence of peroxodisulfate ions. The mechanism of hole injection, cathodic dissolution and electroluminescence with peroxodisulfate ions in acid medium can be explained as shown in Fig. 9.

The previous studies describe the cathodic decomposition of InP in acid medium.[11] At potentials where hydrogen is evolved, the interfacial hydrated indium oxide layer is reduced to metallic indium. Since the bands of InP consist of In and P orbitals, a metallic In is likely to introduce deep surface states, in which electrons and holes recombine non-radiatively.[33] The formation of In metal has been explained as in Ref. 34.

$$InP + 3H^+ + 4H_2O + 3e^- \longrightarrow In + H_3PO_4 + 4H_2$$

The indium layer will be oxidized to In_2O_3 by bringing the electrode potential to 0.0 V vs. SCE. This oxide layer passivates radiationless electron-hole recombination.[31,32,35]

Therefore, the dependence of EL on voltage is not only controlled by hole injection, but also by complex surface properties which affect radiationless recombination. The observation of EL is in apparent contradiction with the expectation that the more negative the electrode potential, the higher the electron density at the surface and thereby the recombination probability. According to this description the EL intensity should monotonically increase with potential. The decrease in EL is ascribed to the formation of In metal. It is well known that in the transition from anodic to cathodic a drastic change of the chemical composition occurs for Ge[37] and GaAs.[38] Here, the surface undergoes a transformation between a stable oxidized and a reduced state. During this transformation, unsaturated surface states (due to dangling bonds) are formed within the band gap that can act as very efficient recombination centers. This cannot exclude the possibility of radiation which would be lying beyond the detection system used. Similar increase of surface recombination has been reported for Ge[39] and GaAs.[17]

According to Fig. 4 the increase in the cathodic potential limit does not change the spectral distribution whereas a change in the EL intensity was observed. The reason for the increase of EL intensity with potential can be explained as the accumulation of the electrons in the conduction band near the surface at higher cathodic biases so that the rate of reduction of the peroxodisulfate ions increases to produce more number of $SO_4^{\cdot-}$ radicals for efficient hole injection into the valence band. From the pulsed potential experiment and the EL intensity vs. concentration it is understood that at higher concentration of peroxodisulfate and the electrode at pulsed potential conditions, it is favorable for the peroxodisulfate ions to get reduced at a faster rate than the reduction rate of the semiconductor itself. EL intensities obtained for the normal redox electrolytes saturate at lower intensities in comparison to peroxodisulfate electrolyte (Fig. 6). The higher intensities obtained in peroxodisulfate electrolyte is explained as follows: According to Gerischer's model the three energy states for peroxodisulfate are represented as $S_2O_8^{2-}$, $SO_4^{\cdot-}$, SO_4^{2-}. Since the $SO_4^{\cdot-}$ species are highly unstable an electron transfer from the valence band is much easier to reduce them. Here, in the case of peroxodisulfate (current doubling reagent) the rate of hole transfer from $SO_4^{\cdot-}$ species into the valence band is faster compared to the rate of hole transfer from the other redox electrolytes. In other words, at higher cathodic step potentials i.e., near the saturation region, the rate of hole transfer from the $SO_4^{\cdot-}$ species to the valence band of InP is competitive to the rate of formation of In metal whereas in the case of normal redox electrolytes the rate of hole injection to the valence band seems to be less competitive.

At lower cathodic pulse potentials the rate of formation of In metal is slower than the rate of hole transfer from the electrolyte species to the valence band of InP. Therefore, we observe a steep rise of EL intensity during pulsed condition in most of the electrolytes used. The different behavior in $Ce(SO_4)_2$ electrolyte may be explained as the potential independent hole injection at lower cathodic pulsed potentials. Moreover, during the formation of an accumulation layer at higher cathodic bias potentials, the potential drop occurs at the Helmholtz double layer so that the position of the band edges is shifted in the cathodic direction. This favors the matching of the energy levels of those redox systems having their energy levels above the valence band edge so that the rate of hole injection is increased. This shift will be of importance for $K_3Fe(CN)_6$ and here, the rate of hole injection can compete with the direct electron transfer from the conduction band. Therefore, it is clear that EL measurements can give very instructive information about the mechanism of electron transfer reactions at semiconductor electrodes as well as their surface properties.

Conclusions

In conclusion, the hole transfer to the valence band of InP is the important step in all the electrolytes studied. The main interesting feature of the EL spectrum of InP electrodes is the band edge emission. The emission is highly controlled by the changes due to surface composition. The effect of increasing the cathodic step potential increases the EL intensity and does not shift the emission edges. This indicates that there are no impurity levels, involved in the radiative processes. Basically, peak shifts are attributed to a kinetic effect involving the rate of charge transfer with the impurity levels. EL observation in various redox electrolytes under pulsed polarization gives more information about the competitive hole transfer process. Presently, this technique using current doubling redox electrolyte is advantageous to probe the surface chemistry as well as the stability of indium phosphide electrodes. An extensition of the luminescence experiments due to minority carrier injection can give valuable information about surface properties and mechanism for electron transfer reactions.

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