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Citation: *Journal of Applied Physics* **57**, 2900 (1985); doi: 10.1063/1.335228

View online: <http://dx.doi.org/10.1063/1.335228>

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Electroluminescence of III-V single-crystal semiconducting electrodes

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(Received 27 August 1984; accepted for publication 9 October 1984)

The luminescence generated by hole injection from an aqueous electrolyte into GaAs and InP has been investigated. Solid-state properties are responsible for the variations encountered in different samples and for most differences observed between photoluminescence and electroluminescence.

INTRODUCTION

The luminescence properties of III-V semiconducting compounds have been thoroughly investigated because of the relevance of solid-state luminescent devices (displays, lasers, etc.) in optical communication systems. A limited number of papers have been published on the properties of luminescent III-V semiconductor-electrolyte junctions. Although the aim of this paper is not to be a review paper, we shall quote in the reference section¹⁻¹¹ the literature that to our knowledge exists up to date on this subject. We shall refer only to the phenomenon of radiative recombination that takes place in the solid electrode because of minority carrier injection from active electrolyte ions, and we shall denominate this phenomenon as electroluminescence (EL), to distinguish it from other forms of luminescence (chemiluminescence, for example, which takes place *in* the electrolyte close to the electrode^{12,13}).

The authors of the present work have already devoted their attention to the electroluminescence properties of *n*-GaAs in different redox electrolytes.^{10,11} In those papers, the emphasis was on the relationship between the specific hole-injecting redox ion and the EL spectrum. Different redox ions are responsible for significantly different EL properties because the overlapping of the filled valence band states with the empty electrolyte levels varies very much with the redox couple potential and with the pH of the solution. Two recent papers have appeared in the meantime, in which the kinetics of the hole-injection process in GaAs is studied exclusively by means of the rotating disk and of the rotating ring-disk technique.^{14,15} The conclusions of these papers are substantially in agreement with ours.

The aim of the present paper is different: We elucidate which is the relationship between the single crystal bulk properties (mainly growth conditions and doping) and the EL spectra. We also examine to which extent the EL spectra differ from the photoluminescence (PL) spectra for the various samples used. In this work we only make use of efficient hole-injecting species, i.e., oxidizing species which scavenge valence band electrons at the diffusion-limited rate, and we disregard those redox couples which have a poor overlapping with the electrode valence band. We show for the first time the EL spectra of a liquid-phase-epitaxial (LPE) *n*-GaAs layer and that of an InP electrode. The last part of this paper is devoted to a short investigation of the influence of surface states on the EL efficiency.

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EXPERIMENTAL TECHNIQUES

The electrolyte jet technique was used in order to guarantee efficient mass transport to the semiconductor electrode. The experimental setup for EL measurements and the luminescence detection system has been already described elsewhere.¹¹ PL spectra were all obtained with dry electrodes in air. In the present set of experiments the photomultiplier tube was either a S-1 EMI 9684 B or a S-20 RCA 31034 A, depending on the spectral range investigated, and the spectra were not corrected to the photomultiplier relative spectral response. The samples used were two *n*-GaAs single crystals (Laser Diode Co.) doped with a Si concentration of $5 \times 10^{17} \text{ cm}^{-3}$ and of $3 \times 10^{18} \text{ cm}^{-3}$, and a *n*-InP single crystal with a nonintentional doping density of $6 \times 10^{15} \text{ cm}^{-3}$ and a resistivity of $0.25 \Omega \text{ cm}$. The LPE *n*-GaAs sample was grown in our laboratories on the $5 \times 10^{17} \text{ cm}^{-3}$ substrate and had a Si dopant concentration of about $5 \times 10^{17} \text{ cm}^{-3}$ and a thickness around $10 \mu\text{m}$. In the electrochemical cell the three-electrode configuration was always used and all potentials will be referred to that of the saturated calomel electrode (SCE). Potentiostatic control of the semiconductor electrode was imposed in all the experiments by means of a P. A. R. 173 and 175 electrochemical apparatus. The electrolytes were prepared shortly before the experiments with triply distilled H₂O and with high purity reagents. All the electrodes, except for the LPE one, were etched in H₂SO₄ : H₂O₂ (1 : 1 by volume) prior to use. In order to measure the EL spectra, the more reproducible technique was found to be the one previously employed by Ellis *et al.*,¹⁶ which consists in short (1-s) forward-bias pulses alternated by longer (9-s) time intervals in which the semiconducting electrode is reverse biased. At the same time, the spectrometer was driven at a constant speed and the photomultiplier output was measured with a Keithley Electrometer. For the measurement of the EL dependence on potential we applied a triangular wave potential cycle (i.e., cyclic voltammetry) to the semiconducting electrode. For the measurement of the time dependence of EL (at a fixed potential) we applied the same forward-reverse asymmetric square-wave potential cycle used in the spectral measurements, but with the spectrometer stopped at a given wavelength. The potential pulse amplitude was chosen manually for each cycling frequency and the EL signal was detected with the photomultiplier connected to a conventional lock-in amplifier. In the PL experiments, the photoexcitation was made by means of a 3 mW He-Ne 632.8-nm monochromatic laser radiation.

RESULTS AND DISCUSSION

A. Band-gap region

The semiconductor excitation process which promotes the e^-h^+ radiative recombination is accomplished either by means of the absorption of a quantum of light (PL) or by means of the injection of holes into the valence band from an oxidizing ion (EL). As shown in Fig. 1(a) the first excitation process takes place mainly in the first layer (with thickness $\sim \alpha^{-1}$) beneath the electrode surface and the last excitation process takes place right at the semiconductor-liquid interface. In the simple model shown in Figs. 1(b) and 1(c), where zero electric field throughout the semiconductor and no surface recombination were assumed, hole diffusion length L (the same for both modes of excitation) and photon penetration depth α^{-1} are compared. The spatial distribution of the diffusing holes within the bulk of the semiconductor can be considered independent of the excitation process only if $L \gg \alpha^{-1}$. However if $L \lesssim \alpha^{-1}$, then the sample slice from

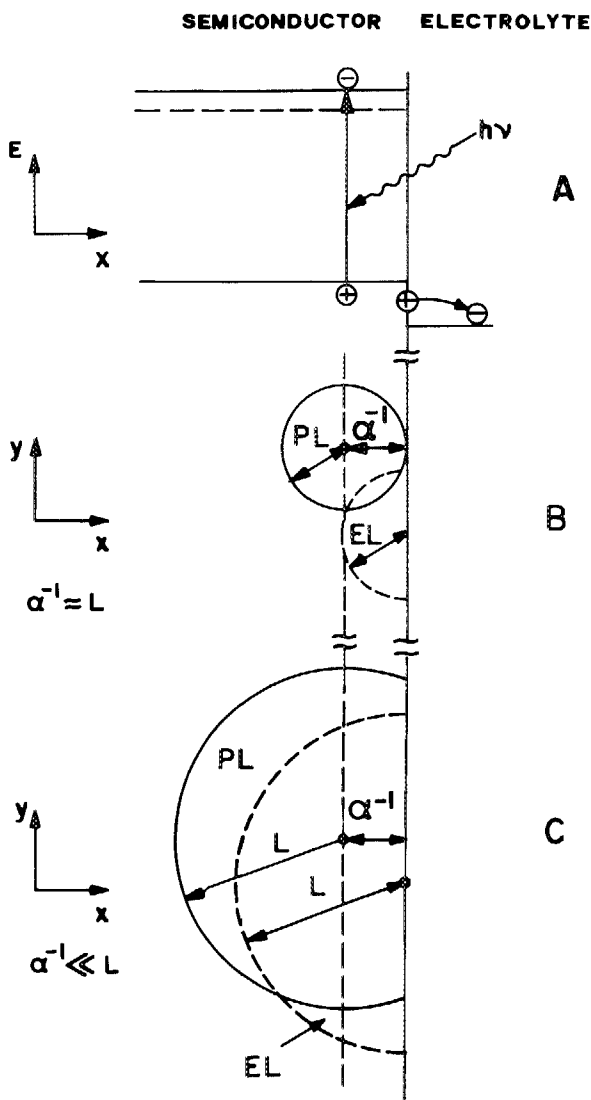


FIG. 1. (A) Band energy diagram for the semiconductor-electrolyte interface, during either illumination or hole injection process; (B) diffusion ranges of the injected minority carriers in the case $\alpha^{-1} \sim L$; (C) the same as (B), but with $\alpha^{-1} \ll L$.

which PL arises is considerably thicker than that where EL radiation is generated. The absorption coefficient and the hole diffusion length for the III-V compounds are fortunately well known, and it is possible to choose samples which satisfy one or the other condition. In GaAs at room temperature for example, L keeps constant at $\sim 2 \mu\text{m}$ up to a doping density of 10^{18} cm^{-3} , but decreases dramatically for higher doping concentration.¹⁷ The value of α^{-1} at 632.8 nm, on the contrary, is $\sim 0.3 \mu\text{m}$ regardless of the doping density at least up to $5 \times 10^{18} \text{ cm}^{-3}$.^{17,18} According to our former model, samples with doping density of at least $3 \times 10^{18} \text{ cm}^{-3}$ should therefore show an EL spectrum which is somewhat different from its corresponding PL spectrum.

In Fig. 2 the EL and PL relative intensities are plotted in a logarithmic scale as a function of the photon energy, in the range from 1.42 to 1.62 eV, for two different n -GaAs samples. The shift of the peak position in Fig. 2 is due to the participation of electron states well into the conduction band; the broadening of the emission band is also due to impurity banding, tailing of states and variations in the absorption edge with doping. Both effects are indeed already well known for the III-V semiconducting compounds.¹⁹ The EL and PL spectra of the $5 \times 10^{17} \text{ cm}^{-3}$ sample are only slightly different. However, a clear separation in the high-energy tails of the PL and EL spectra of the $3 \times 10^{18} \text{ cm}^{-3}$ sample is observed. According to the model in Fig. 1, the photogenerated holes in the $3 \times 10^{18} \text{ cm}^{-3}$ sample should diffuse much deeper into the bulk than the electrolyte-injected holes. This fact implies in a stronger reabsorption effect of the photons coming from the recombination of the photo-

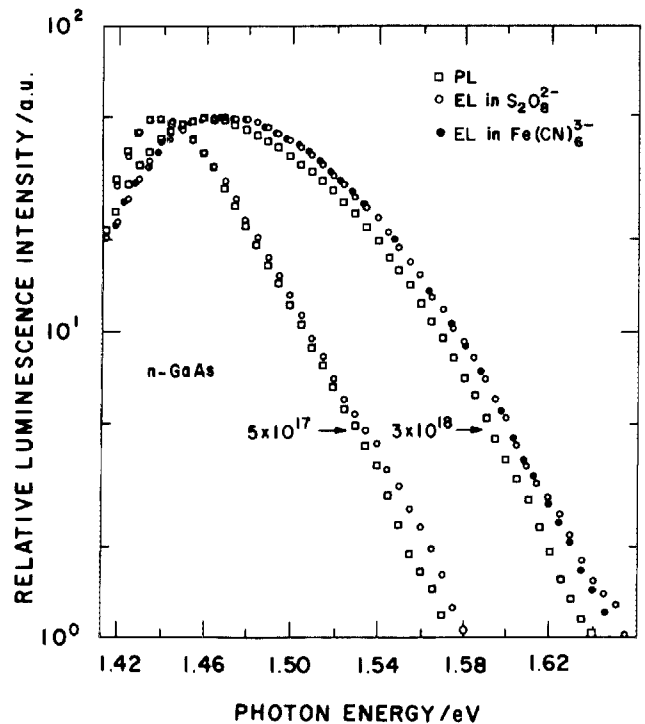


FIG. 2. Logarithmic plot of the luminescence intensity vs photon energy for two different n -GaAs samples. PL is excited by an He-Ne laser; EL is obtained by pulsing the electrode potential between 0.0 V (1 s) and -1.75 V (9 s) in $0.5 M$ NaOH + $0.1 M$ $\text{Na}_2\text{S}_2\text{O}_8$ (open dots) and in $0.5 M$ NaOH + $0.05 M$ $\text{K}_3\text{Fe}(\text{CN})_6$ (closed dots).

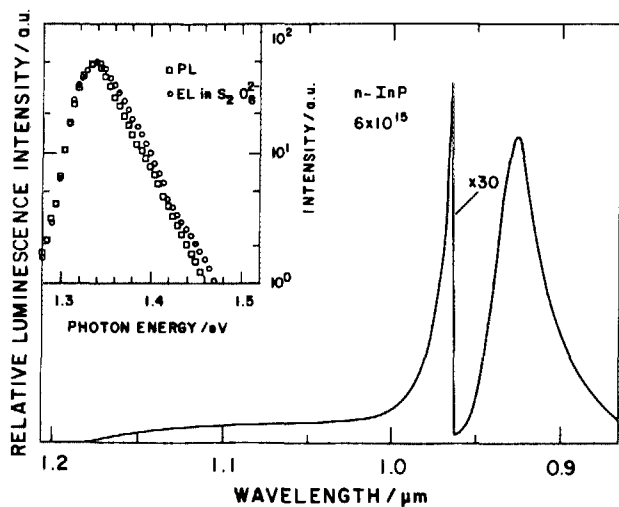
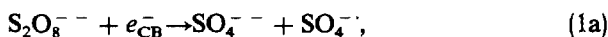


FIG. 3. Linear photoluminescence intensity vs wavelength plot for an *n*-InP sample. In the inset, logarithmic plot of the band-edge luminescence region. PL is excited by an He-Ne laser; EL is obtained by pulsing the electrode potential between 0.0 V (1 s) and -1.6 V (9 s) in 0.5 M NaOH + 0.1 M Na₂S₂O₈.

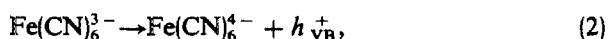
generated holes, mainly at shorter wavelengths. A similar mechanism was already proposed by Ellis for the II-VI semiconducting electrodes. With the III-VI compounds, however, samples with different doping density can be easily chosen in order to vary the value of L , so that the differences between PL and EL spectra can be conveniently analyzed. Note that the EL spectrum obtained with the $\text{Fe}(\text{CN})_6^{3-}$ ion is practically the same as that obtained with the $\text{SO}_4^{\cdot-}$ radical. We remember that the oxidizing $\text{SO}_4^{\cdot-}$ radical is generated by the reaction with conduction band electrons



and injects holes according to the reaction⁴



The reduction of the $\text{Fe}(\text{CN})_6^{3-}$ ion, on the other hand, is a one-electron reduction reaction



and is a much simpler electrochemical reaction than the sum of reactions (1a) and (1b). The physical consequence is that the energy at which the charge transfer process takes place can be better evaluated in the case of reaction (2) than in the case of reaction (1b). Both $\text{SO}_4^{\cdot-}$ and $\text{Fe}(\text{CN})_6^{3-}$ species however are likely to inject holes deep into the valence band ("hot holes"), which rapidly thermalize, diffuse, and recombine producing the EL spectra as shown in Fig. 2.

Analogous remarks can be made for the EL and PL spectra obtained for the *n*-InP sample (see Fig. 3). Although we do not have InP samples with different doping densities, we can however reasonably presume that the effect of the dopant concentration would be analogous to that observed in GaAs.

B. Sub-band-gap region

It is interesting to observe that the PL spectrum of InP (Fig. 3) does not show any sub-band-gap emission. The same is observed in EL, both with the $\text{S}_2\text{O}_8^{2-}$ and the $\text{Fe}(\text{CN})_6^{3-}$

ions. Deep states where e^-h^+ pairs can radiatively recombine do not exist in our InP sample in high enough concentration, at least not with such an energy which is compatible with the photon energy range of our detection system.

This is not true, however, for our melt-grown *n*-GaAs samples that show a very broad band peaking at ~ 1100 nm both in the EL (Fig. 4, upper curve) and in the PL spectra.¹¹ This sub-band-gap emission band has been attributed to radiative transitions from shallow donor states to deep (~ 0.3 -eV from the valence band) acceptor states created by gallium vacancies.¹¹ One can easily see, in the lower curve of Fig. 4, that the states which are responsible for the sub-band-gap emission are in much smaller concentration in the LPE GaAs sample. This observation is relevant for the research in electrolyte electroluminescence since in many earlier papers it has been claimed that sub-band-gap emission could arise from recombination assisted by surface states. Since the same kind of surface states can presumably be found both for a melt-grown and for a LPE GaAs single crystal, the attribution of sub-band-gap emission to surface states cannot be correct.

Another interesting question can be answered by means of detection of the sub-band-gap luminescence: How long does a few microns thick semiconducting layer last before it gets corroded in the aqueous electrolyte? We have observed that, when the electrolyte is $\text{S}_2\text{O}_8^{2-}$, after several hours of continuous operation there is no detectable sub-band-gap signal from the GaAs substrate underlying the thin LPE layer. This means that the LPE layer has not been corroded at a rate comparable to the rate of hole injection from the $\text{SO}_4^{\cdot-}$ radicals. If such an experiment would be repeated with the $\text{Fe}(\text{CN})_6^{3-}$ ion, the LPE layer would be washed out in a few minutes. It is very well known that $\text{Fe}(\text{CN})_6^{3-}$ alkaline solutions are etchants of GaAs,²⁰ and in fact we do confirm this with our sub-band-gap luminescence experiments. The

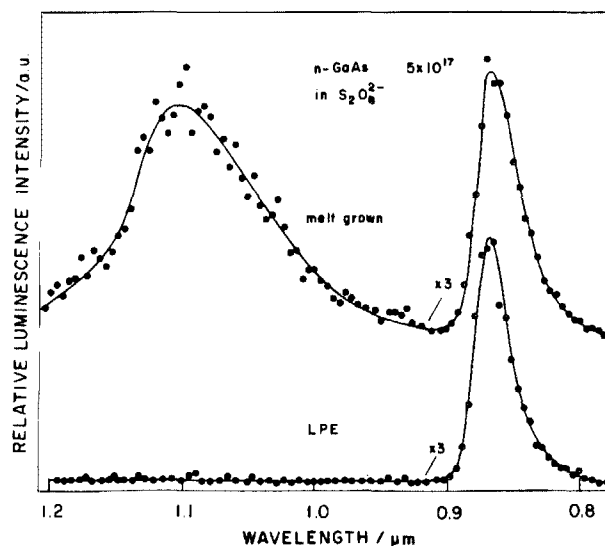


FIG. 4. Linear electroluminescence intensity vs wavelength plots for two different *n*-GaAs samples. The upper curve is obtained with a sample grown from the melt. The lower curve is obtained with a LPE layer on top of the former sample. Both samples have about the same dopant concentration. EL is obtained by pulsing the electrode potential between 0.0 V (1 s) and -1.75 V (9 s) in 0.5 M NaOH + 0.1 M Na₂S₂O₈.

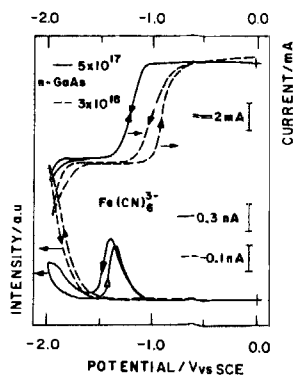


FIG. 5. Cyclic current vs potential curves (upper part) and simultaneous electroluminescence vs potential curves (lower part) for two different n -GaAs samples. Potential sweep rate 20 mV s^{-1} . Electrolyte $0.05 \text{ M Fe(CN)}_6^{3-} + 0.5 \text{ M NaOH}$.

only way GaAs does not get corroded in Fe(CN)_6^{3-} solutions is when it is polarized in such a cathodic potential that the diffusion-limited current is reached (e.g., -1.75 V in Fig. 5). The dependence of the corrosion rate on the electrode potential was already discussed in former works,^{10,21} but will be treated again in the next section because of its implications on EL intensity.

C. Electrode potential dependence of the band-gap luminescence

It has been previously discussed¹⁰ that the electrode potential should be set close to the flat-band potential or should produce an accumulation layer in the semiconductor surface if an intense EL signal is desired. Otherwise a potential barrier exists which confines the thermalized injected holes into the surface layer and repels the conduction electrons deeper into the bulk, therefore preventing strong e^-h^+ radiative recombination. The flat-band potential of n -GaAs lies around -1.0 – -1.2 V in a solution with 0.5 M OH^- .²² The expectation that EL arises only for $V < -1.0 \text{ V}$ is confirmed by the experiments shown in Figs. 5 and 6. Furthermore, several details in the I - V (current vs potential) and simultaneous EL - V (electroluminescence vs potential) curves deserve our attention

(1) The cathodic currents are larger and steeper with the Fe(CN)_6^{3-} ion than with the $\text{S}_2\text{O}_8^{2-}$ ion: the electroreduction of $\text{S}_2\text{O}_8^{2-}$ is in fact a slower reaction than the electroreduction of Fe(CN)_6^{3-} .

(2) The cathodic currents start much earlier for the sample having higher doping density, because in this sample a larger amount of charge carriers is available and because the semiconductor space charge layer is very thin and easily tunneled.

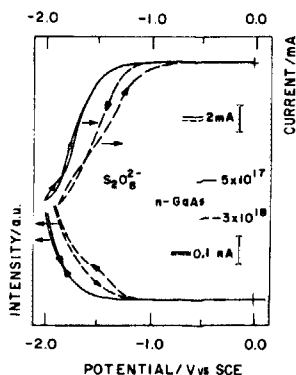


FIG. 6. The same as Fig. 5, but with an $0.1 \text{ M Na}_2\text{S}_2\text{O}_8 + 0.5 \text{ M NaOH}$ electrolyte.

(3) The EL - V curves in the $\text{S}_2\text{O}_8^{2-}$ electrolyte are nearly symmetrical to the I - V curves, but this is not the case in the Fe(CN)_6^{3-} electrolyte.

The EL - V curves in the last electrolyte (Fig. 5) have other striking features: they differ between each other, both in shape and in intensity, mainly in the potential region between -1.0 and -1.5 V . Decker, Pettinger, and Gerischer have already shown in a previous publication¹⁰ that for GaAs samples with donor density of the order of 10^{17} cm^{-3} both I and EL rise exponentially in the potential range which is close to the flat-band potential. Moreover it is noticeable that exactly at the potential where the diffusion-limited current (I_{lim}) is reached the EL intensity drops for the $5 \times 10^{17} \text{ cm}^{-3}$ sample [see Fig. 5 and also Fig. 6 in Ref. (10)]. It should be remembered that when I_{lim} is reached, conduction band electrons start to accumulate at the electrode surface. One can therefore find a good reason for the abrupt quench in the EL intensity: in the potential range where $|I| < |I_{\text{lim}}|$ there is a corrosion current $-I_{\text{corr}} = I_{\text{lim}} - I$ that keeps the electrode surface under a continuous etching process. However when I_{lim} is reached, the surface is no more renewed and, in the presence of the accumulated electrons, it undergoes a physicochemical transformation that increases the surface recombination velocity quenching the EL . According to the Gerischer,²³ an unsaturated Ga-hydride layer is probably formed at this point. However why does the $3 \times 10^{18} \text{ cm}^{-3}$ sample not show any of these features? The more likely explanation is that in this sample the injected holes, due to their much shorter diffusion length, cannot escape from radiationless surface recombination unless a strong electric field is applied (i.e., large negative potential).

The next step is then to set up an experiment that could indicate how much time is required for this physicochemical surface transformation to take place. Using the asymmetric square-wave potential cycling technique already described, we follow the EL intensity by synchronous detection as a function of the pulse height (ΔV) and of the cycling frequency (Fig. 7). Interestingly, we find that the ac EL - V curves ($5 \times 10^{17} \text{ cm}^{-3}$ sample) are very similar to the dc EL - V curves in Fig. 5 as long as the frequency is below 500 Hz . Between 1 and 5 kHz the EL - V shape suddenly changes and approaches the exponential behavior previously observed although only in the potential range close to the flat-band potential.¹⁰ We deduce therefore that the surface transformation described above takes place in a time interval of the order of 0.1 ms (taking into account the square-wave asymmetry).

Surface modifications can also be intentionally provoked. As an example, we have introduced $10^{-5} \text{ M Bi(NO}_3)_3$ in a solution of $0.1 \text{ M Na}_2\text{S}_2\text{O}_8 + 0.5 \text{ M NaOH}$, while the EL intensity from the pulsed ($1 \text{ s}-0.4 \text{ V}$, $9 \text{ s}-1.9 \text{ V}$) $5 \times 10^{17} \text{ cm}^{-3}$ GaAs electrode was followed at a fixed wavelength (856 nm). In about 40 s the EL intensity had dropped to 25% of its initial value, while in 20 s the current during the pulse had increased by a factor ~ 1.7 . Nearly no effect was observed both in the current and in the EL intensity when RuCl_3 was added to the electrolyte. It has been already reported by other authors²⁴ that the treatment of GaAs electrodes with Bi^{3+}

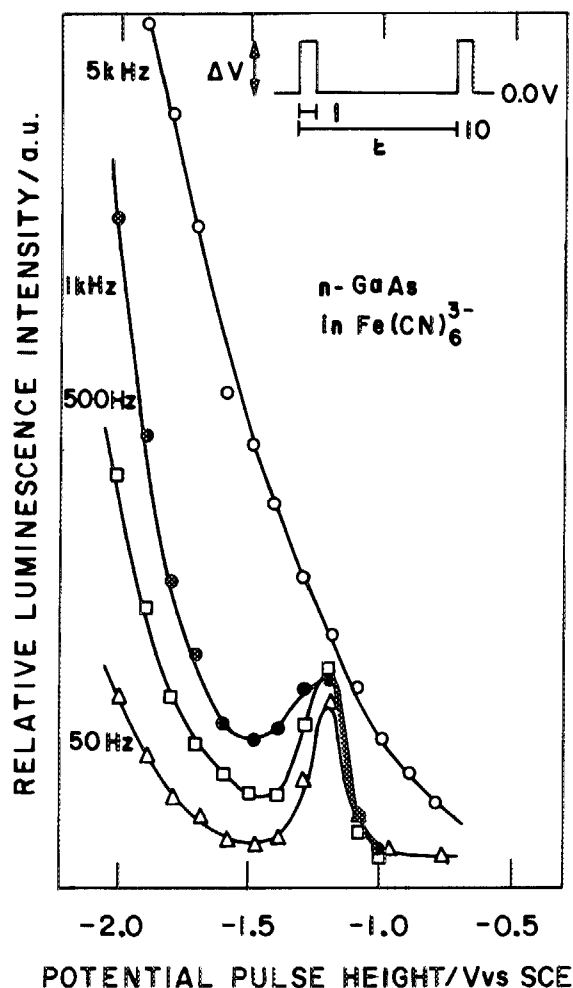


FIG. 7. ac electroluminescence intensity vs potential pulse height plots for a n -GaAs sample ($5 \times 10^{17} \text{ cm}^{-3}$) in a $0.05 \text{ M Fe(CN)}_6^{3-} + 0.5 \text{ M NaOH}$ electrolyte, as a function of the cycling frequency. In the upper part, the shape of the square-wave pulse is indicated.

ions has a negative effect on the photocell efficiency, this effect being attributed to the introduction of surface states deep in the band gap. These states correspond to a weakening of the surface chemical bonds.^{25,26} Since after the adsorption of Bi^{3+} on the GaAs surface the cross section for surface radiationless recombination of electron and holes is expected to increase, at the same time the cross section for bulk radiative recombination of electron and holes should decrease. This is in fact shown by our experiment.

Some ambiguity could be left since during the cathodic pulse metallic Bi^0 could be deposited. To solve this ambiguity in a second experiment the electrode potential was not pulsed during 40 s after the Bi^{3+} addition, but still a significant decrease of the EL intensity in the first pulses after the Bi^{3+} addition was observed, when compared with EL before the addition. We conclude that we have been able to introduce accidentally surface states which quench the band edge luminescence. In a previous publication²⁷ we have shown that it is also possible to perform the opposite experiment, i.e., to increase band-edge EL intensity by decreasing the

density of surface radiationless recombination centers with photoetching. This was only possible, however, with polycrystalline CdSe thin film semiconducting electrodes.

CONCLUSIONS

In this work, we have elucidated the influence of the single crystal bulk properties on the electroluminescence processes. An important conclusion is that in many III-V compound electrodes the differences between EL and PL spectra are very tiny, especially if comparable excitation rates and samples with large minority carrier diffusion lengths are used. We have shown the effect of the crystal growth technique on the EL spectra and we have discussed the effect of surface intentional and unintentional modification on the EL intensity. We have not found any experimental evidence that radiative recombination can take place at surface states located at the semiconductor-electrolyte interface.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of FINEP and CNPq.

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