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Further Studies of Electroluminescence Spectra of the *n*-GaP Semiconductor Electrode in Relation with the Surface-trapped Holes

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Electroluminescence spectra of an *n*-type gallium phosphide (*n*-GaP) electrode caused in the presence of oxidants such as $[Fe(CN)_6]^{3-}$ and $S_2O_8{}^{2-}$ were measured as functions of the electrode potential, the solution pH, and the kind of crystal faces. The electroluminescence spectra consisted of two bands; one was assigned to arise from electronic transitions in the bulk and the other from those at the surface. It was found that the position and the spectral shape of the luminescence band arising from the surface were quite independent of various experimental conditions, while its intensity was strongly dependent on them. These results were explained well by the view that the luminescence band is caused by "surface-trapped holes" acting as a precursor of anodic dissolution reaction of the electrode, as proposed previously. The physicochemical model of the surface-trapped hole was discussed on the basis of the above results.

Extensive work has been done on the semiconductor photoelectrochemical cells in relation with solar energy conversion.[1–4] The main difficulty in this method arises from the fact that most of the available semiconductors with moderate bandgaps are more or less photocorrosive in electrolyte solutions.

The photoelectrochemical stability of semiconductor electrodes was first discussed on the basis of the thermodynamic decomposition potentials,[5–8] and later, much attention has been paid to the kinetic stability of the electrodes.[1,3–5,8] It is very important to understand the physicochemical nature of holes and electrons at the surface, which act as precursors or intermediates of the electrode reactions. Many workers have often pointed out the importance of surface states as arising from surface defects or impurities,[3,4] but the detailed nature of them on a molecular level has still been quite obscure.

We studied electrochemical and luminescent properties of an *n*-type gallium phosphide (*n*-GaP) electrode, and proposed a concept of "surface-trapped holes" as a precursor of various anodic reactions of the electrode.[9] We also studied electro- and photoluminescence spectra of other *n*-type semiconductors such as *n*-CdS, *n*-ZnO, and *n*-TiO_2, and reported that some of the luminescence bands were interpreted as arising from the surface-trapped holes similar to those of *n*-GaP.[10] In the present paper we will report the results of further detailed studies on the electroluminescence spectra of the *n*-GaP electrode.

Experimental

Electrodes were prepared by using single crystal wafers of *n*-GaP, cut perpendicular to the (111)-axis of the crystal, in a similar way to reported before.[9a] They were etched in hot aqua regia for about 20 s before use. The (111)-face (Ga-face) and the $(\bar{1}\bar{1}\bar{1})$-face (P-face) were distinguishable by microscopic inspection of the etched surface.[9a]

Electroluminescence was emitted when the *n*-GaP electrode was kept at cathodic potentials by use of a potentiostat in aqueous solutions containing an oxidant such as $S_2O_8{}^{2-}$ or $[Fe(CN)_6]^{3-}$. In general the luminescence arises *via* radiative recombination between holes injected by the oxidant in solution and electrons in the conduction band. The luminescence spectra were measured by using a Jobin-Yvon H20 monochromator and an HTV R316 photomultiplier cooled at −20 °C. The observed spectra were corrected with reference to the spectral sensitivity of the photomultiplier, which was measured by use of an Eppley thermopile. The peak wavelengths of the corrected spectra agreed well with those reported by other workers.[11,12]

Luminescence (or photoluminescence) was also emitted when the electrode in an electrolyte solution without oxidants was illuminated at the 365 nm band by use of a 500 W high pressure mercury lamp combined with a Shimadzu-Bosch-Lomb monochromator and appropriate light filters. The luminescence spectra were measured with the same detector system as used for the electroluminescence spectra.

The current-potential curves were obtained with a Nikko-Keisoku NPGS-301 potentiostat. Solutions were prepared by use of deionized water and reagent grade chemicals. They were stirred magnetically and deaerated by bubbling nitrogen during experiments. The pH of the solutions in the range of 3 to 11 was controlled by using an appropriate buffer mixture; acetate, phosphate, borate, or carbonate. The concentration unit, mol/dm^3, is abbreviated as M in the present paper.

Results

In Fig. 1, electroluminescence spectra from the Ga-face (——) and the P-face (—·—) of an *n*-GaP electrode caused by an oxidant, $[Fe(CN)_6]^{3-}$, and that from the Ga-face (----) caused by an oxidant, $S_2O_8{}^{2-}$, are shown, together with a photoluminescence spectrum (······). The electroluminescence spectra from the Ga- and the P-face caused by $[Fe(CN)_6]^{3-}$ almost agree with each other except for a slight difference in a swelling near 1.4 eV. The position and the spectral shape of the photoluminescence spectrum were nearly independent of the electrode potential, the solution pH, and the kind of the crystal face.

In Fig. 2, the potential dependence of the electroluminescence spectra from the Ga-face caused by $[Fe(CN)_6]^{3-}$ at pH 5.5 is shown. It is seen that the spectra hardly change with the electrode potential except for slight differences in the extent of the swelling near 1.4 eV. Similar results were observed in solutions of other pH values, and also for the spectra from the P-face. The electroluminescence spectra caused by $[Fe(CN)_6]^{3-}$ also hardly depended on the solution pH except for the slight difference in the swelling near 1.4 eV, as seen from a comparison of Figs. 1 and 2.

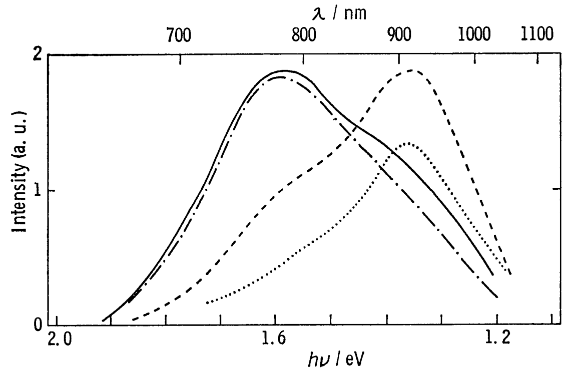

Fig. 1. Electro- and photo-luminescence spectra of an *n*-GaP electrode: Spectra from the Ga-face (——) and the P-face (—·—) generated at −2.2 V *vs.* SCE in a 0.1 M NaOH aqueous solution containing 0.1 M $K_3[Fe(CN)_6]$ and 0.1 M $K_4[Fe(CN)_6]$; that from the Ga-face (----) generated at −1.9 V *vs.* SCE in a 0.1 M NaOH solution containing 0.5 M $Na_2S_2O_8$; and that from the Ga-face (······) generated by illumination in a 0.1 M NaOH solution.

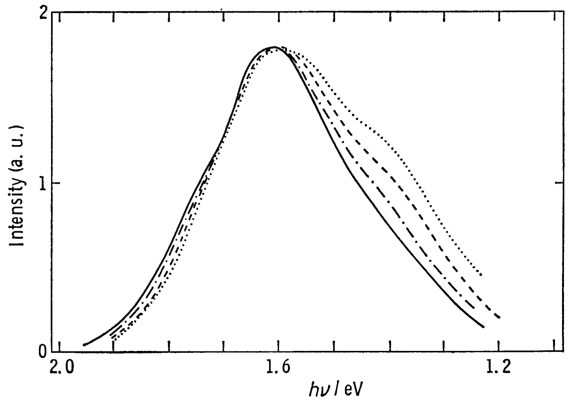

Fig. 2. Electroluminescence spectra from the Ga-face of an *n*-GaP electrode in a solution containing 0.1 M $K_3[Fe(CN)_6]$ and 0.1 M $K_4[Fe(CN)_6]$ at pH 5.5. The spectra were measured at −1.75 V *vs.* SCE (—·—), −1.60 V (——), −1.40 V (----), and −1.35 V (······).

In Fig. 3, the potential dependence of the peak intensity (I) of the electroluminescence spectra in a $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ solution at pH 4.4 is compared with that of the dark cathodic current (j). These results were obtained by scanning the potential cyclically in a limited range of the potential. The luminescence intensity *vs.* potential curves depended on both the scanning rate and the scanned range of the potential, though the general patterns were rather similar to each other.

Similar experiments were made in solutions of various pH. The results at pH 12.8 are shown in Fig. 4.

Discussion

In a previous letter,[10] it has been concluded that the photoluminescence spectrum of the *n*-GaP electrode arises mainly from electronic transitions in the bulk of the semiconductor, while the electroluminescence spectra caused by $[Fe(CN)_6]^{3-}$ arise mostly from electronic transitions at the surface. It has also been concluded[10] that the swelling of the electroluminescence spectra caused by $[Fe(CN)_6]^{3-}$ appearing at 1.4 eV (Figs. 1 and 2), where the photoluminescence peak just lies, is due to a small contribution of the luminescence band arising from the bulk.

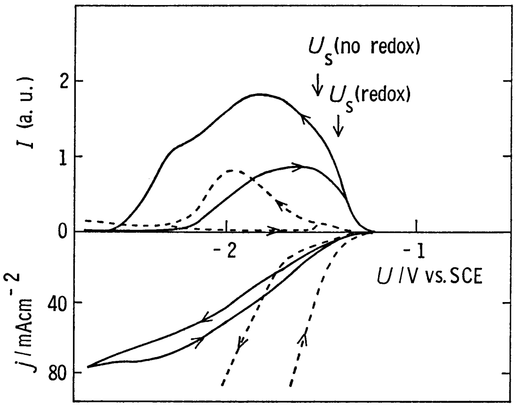

Fig. 3. Potential dependences of the peak intensity of the electroluminescence spectra (I) and the cathodic current (j) for the Ga-face (——) and the P-face (----) in a solution containing 0.1 M $K_3[Fe(CN)_6]$ and 0.1 M $K_4[Fe(CN)_6]$ at pH 4.4.
The scan rate is 200 s/V. The U_S values indicated by arrows are for the Ga-face. The U_S (no redox) for the P-face is almost the same as that for the Ga-face.[9b)]

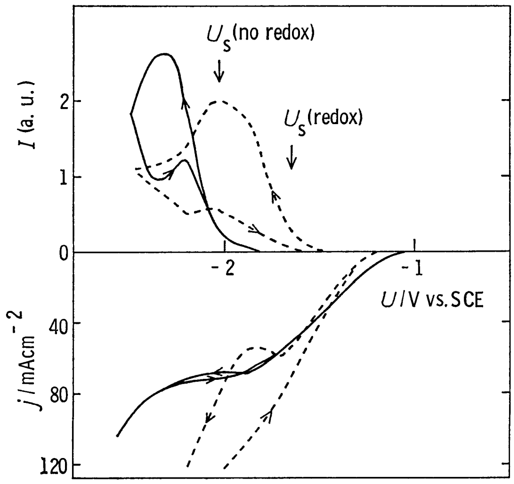

Fig. 4. Potential dependences of the peak intensity of the electroluminescence spectra (I) and the cathodic current (j) for the Ga-face (——) and the P-face (----) in a 0.1 M NaOH solution (pH 12.8).
Other conditions are the same as in Fig. 3.

The electroluminescence spectrum caused by $S_2O_8^{2-}$ (a broken line in Fig. 1) shows a strong peak at 1.36 eV and a shoulder near 1.6 eV, suggesting that the luminescence spectrum arises mostly from the bulk, contrary to the spectrum caused by $[Fe(CN)_6]^{3-}$. According to the literature,[11,12)] the $S_2O_8^{2-}$ ions are first reduced by electrons in the conduction band, and the resulting radical, $SO_4^{-}\cdot$, acts as a very strong oxidant. The above result can therefore be explained by assuming that holes injected by the $SO_4^{-}\cdot$ radicals are quite hot and a large part of them can diffuse into the bulk.

As mentioned in the preceding section, the electroluminescence spectra caused by $[Fe(CN)_6]^{3-}$ hardly change with the electrode potential, the solution pH, and the kind of the crystal face, except for the differences in the extent of the swelling near 1.4 eV, *i.e.*, the extent of the contribution of the luminescence band arising from the bulk. This means that the position and the spectral shape of the luminescence band arising from the surface are quite independent of these experimental conditions. The changes of the contribution of the luminescence band arising from the bulk with the electrode potential and the pH can be explained qualitatively by taking account of the changes of the surface density of the electrons in the conduction band as well as those of the initial energy of the injected holes.

The intensity of the electroluminescence spectra at *ca.* 1.6 eV (*i.e.*, the intensity of the luminescence band arising from the surface), on the contrary, depends strongly on the electrode potential, the pH, and the kind of the crystal face, as seen in Figs. 3 and 4. In these figures U_s(redox) is a potential which was determined previously from the intercept of a Mott-Schottky plot with the abscissa,[9b)] and thus $-eU_s$(redox) approximately indicates the energy of the conduction band edge at the electrode surface in contact with the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ solution under anodic bias.[9a)] The U_s value in the absence of the redox couple, designated as U_s(no redox), is also included in Figs. 3 and 4. Since the deviation of U_s(redox) from U_s(no redox) was attributed to the accumulated surface-trapped holes and/or oxidative surface intermediates produced during the reaction of the holes with the solution,[9b,c)] U_s(redox) is thought to approach U_s(no redox) as the electrode potential is shifted to the negative and the surface density of the electrons in the conduction band increases. Accordingly, we can roughly estimate that the flatband potential of *n*-GaP lies around U_s(no redox) even in the presence of the redox couple.

Based on this argument on the U_s and the previously reported assignment of the electroluminescence spectra peaked at 1.6 eV as being a recombination luminescence between the surface-trapped holes and the electrons in the conduction band,[9b,c)] the main features of the results shown in Figs. 3 and 4 can be explained qualitatively as follows.

As seen in Fig. 3, when the electrode potential is swept from positive to negative in an acidic solution, the electroluminescence spectra from the Ga-face start to appear at a potential slightly less negative than U_s(no redox), and reach the maximum at a potential slightly more negative than the U_s(no redox), then decrease rather rapidly at more cathodic potentials. The slight shift of U_s(redox) from U_s(no redox) shown in Fig. 3 suggests that the surface-trapped holes and/or oxidative surface intermediates are accumulated under anodic bias only to a small extent in this case.[9b)] Since the surface density of the electrons in the conduction band at anodic potentials are negligibly small, most of the surface-trapped holes formed through the hole injection by the oxidant, $[Fe(CN)_6]^{3-}$, should only be reduced again by the reductant, $[Fe(CN)_6]^{4-}$, at such potentials.[9b)] The initial increase of the luminescence intensity when the electrode potential is swept from positive to negative can then be attributed to the increase of the surface density of the electrons in the conduction band. The decrease of the intensity at the more cathodic potentials can be explained by assuming that when the surface density of the electrons in the conduction band becomes very high, the electrode is covered with chemically reduced surface species, with which the injected holes or the oxidant in solution react effectively, not forming the surface-trapped holes.

The onset potential of the cathodic current at the Ga-face in an acidic solution lies very close to a potential at which the electroluminescence starts to appear (Fig. 3). Therefore, the cathodic current near the onset potential can be explained as due mostly to the electron transfer from the conduction band into the $[Fe(CN)_6]^{3-}$ ions *via* the injected holes. The direct electron transfer from the conduction band to the oxidant may partly contribute to the current. At potentials more negative than *ca.* −2.0 V *vs.* SCE, evolution of gas, most probably, hydrogen gas, was observed at the electrode surface. Since the hydrogen evolution is thought to proceed with adsorbed hydrogen atoms (or a kind of surface hydrides) as a reaction intermediate, the above fact means that a kind of surface hydrides is formed at highly negative potentials. This is in harmony with the above argument that the decrease in the electroluminescence intensity at highly negative potentials is due to the formation of certain chemically reduced surface species. The formation of surface hydrides at cathodic potentials was also discussed in the literature.[13–15)]

The electroluminescence intensity *vs.* potential curve for the Ga-face shows hysteresis as seen in Fig. 3. From the discussions made so far, it is very plausible that the chemical structure of the electrode surface changes with the electrode potential from the more or less oxidative structures in an anodic region to the reductive ones in a cathodic region. The hysteresis can then be explained as being due to that the sweep rate of the electrode potential is faster than the rate of the chemical change at the electrode surface. This explanation is supported by a fact that the hysteresis becomes more prominent as the sweep rate becomes high.

The electroluminescence intensity *vs.* potential curve for the P-face in an acidic solution is rather similar in its essential pattern to that for the Ga-face (Fig. 3), and therefore can be explained similarly. The minor differences may be attributable to the differences in the quantity and the reactivity of the oxidative or reductive surface intermediates between the two faces.

The onset potential of the cathodic current at the Ga-face in a high pH solution lies considerably more positive than U_s(no redox) (Fig. 4). As reported in a previous paper[9b)] and also seen from the large shift of U_s(redox) from U_s(no redox) shown in Fig. 4, the surface-trapped holes and, especially, the oxidative surface intermediates produced *via* the reaction of the holes with the solution are thought to be accumulated in a large amount at the electrode surface under anodic bias in the case where it is in contact with the $[Fe(CN_6)]^{3-}/[Fe(CN)_6]^{4-}$ solution of high pH. The above-mentioned cathodic current can then be explained by assuming that some of the accumulated oxidative surface intermediates (possibly certain surface radicals[9a)]) act as effective mediators for the electron transfer from the conduction band to the oxidant in solution.

The electroluminescence spectra from the Ga-face in a high pH solution start to appear at a potential only slightly more positive than U_s(no redox), contrary to the cathodic current (Fig. 4). Since the oxidative surface intermediates are accumulated much at the electrode surface in this case, as mentioned above, some of the $[Fe(CN)_6]^{3-}$ ions coming to the surface may be reduced by the conduction band electrons trapped at the accumulated surface intermediates, not causing the hole injection. The holes injected by the $[Fe(CN)_6]^{3-}$ ions may also be reduced by the electrons trapped at the surface intermediates. These considerations imply that the surface-trapped holes are not effectively formed in the presence of largely accumulated surface intermediates. Accordingly, the electroluminescence is thought to become detectable only when the surface density of the electrons in the conduction band becomes considerably high, *i.e.*, the electrode potential approaches U_s(no redox).

The onset potential of the cathodic current at the P-face lies less positive than that at the Ga-face (Fig. 4). The potential at which the electroluminescence starts to appear at the P-face also lies more positive than that at the Ga-face (Fig. 4). These results can be explained, according to the above arguments on the results for the Ga-face, by assuming that the density of the accumulated surface intermediates at the P-face is less than that at the Ga-face. This explanation is in agreement with a reported result[9b)] that the shift of U_s(redox) from U_s(no redox) at the P-face is smaller than that at the Ga-face.

It is interesting to note in Fig. 4 that when the electrode potential is swept from positive to negative, the cathodic current at the P-face once decreases in the potential range where the electroluminescence just becomes strong. This can be explained by assuming that when the radiative recombination between the surface-trapped holes and the electrons in the conduction band becomes appreciable, the density of the surface intermediates (*i.e.*, the mediators of electron transfer, which are produced *via* the surface-trapped holes) decreases. Similar behavior was generally observed for both the Ga- and P-face in solutions of pH 6 to 11, *i.e.*, in cases where the density of the accumulated surface intermediates is estimated to be moderate. The large cathodic currents at the P-face on potential sweeps from negative to positive in Fig. 4 might be mediated by reductive surface species produced at cathodic potentials.

It is finally noted that the large differences in the dependence of the luminescence intensity on the potential between the Ga- and the P-face observed at any pH (Figs. 3 and 4) are in a sharp contrast to the similarities of the position and the spectral shape of the luminescence spectra (Fig. 1). The difference in the dependence of the luminescence intensity on the potential should imply that the luminescence spectra from the Ga- and the P-face arise from the surface of different chemical structures. The spectral similarity therefore shows that the luminescent species (*i.e.*, the surface-trapped holes) exist in such a way that their energy is almost independent of detailed differences in surface chemical structures between the Ga- and the P-face. This is difficult to explain if the surface-trapped holes are assumed to be holes trapped at certain surface sites such as kinks, steps, *etc.* The above result might rather be reasonably explained by a previously proposed model for the surface-trapped hole[9b,c)] that it is an electron deficiency delocalized over a relatively wide range of the crystal lattice inside the surface. The energy of such an electron deficiency should not be affected much by the surface chemical structure.[16)] The slight deviation of its energy from the valence band edge at the surface (≈0.6 eV[9b,c)]) is thought to be mainly attributable to the distortion of the crystal lattice at the surface.

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16) If the surface of the *n*-GaP electrode is assumed to be covered with a very thin hydroxide or oxide layer,[9a)] the energies of the valence electrons in the surface Ga–P bonds should lie relatively deep due to the stabilization (or the inductive effect) by adjacent, electronegative oxygen atoms. This implies that the electron deficiency (hole) is little distributed on the Ga–P bonds just at the surface and its energy is hardly affected by the surface chemical structure.