experiment successfully. A relatively short delay (50 ms) between the 90° ^1H pulse and the first 90° ^{13}C pulse is close to optimum from a sensitivity point of view, but a longer delay (100 ms) makes the suppression of protons not coupled to ^{13}C easier. When working in D_2O solutions, we find accurate temperature control important for elimination of the unwanted ^1H signals. Because sample spinning modulates the quality factor (Q) of the receiver coil, better suppression of unwanted signals is usually obtained if the sample is not spun.

Discussion

Our study of coenzyme B_{12} illustrates the power of some of the newer types of 2D NMR techniques. Determination of long-range ^1H–^{13}C connectivity is crucial for providing complete proton and carbon assignments. This experiment provides information very similar to the 2D INADEQUATE experiment[47,48] but is several orders of magnitude more sensitive. In addition, this method allows the bridging of heteroatoms, not easily achieved with the INADEQUATE experiment. Assignment of the ^1H spectrum of coenzyme B_{12} was made using the new HOHAHA method in combination with the COSY and the spin-locked NOE experiments. However, some remaining ambiguities (for example, distinguishing between the C46 and C47 methyl protons) could only be resolved either by comparison of NOE data with the X-ray crystal structure or by using the long-range ^1H–^{13}C connectivity.

The results of previous studies led to correct but incomplete (about 50%) ^1H signal assignments. However, a relatively high number of incorrect ^{13}C signal assignments were made. It has been shown here, that unambiguous assignments of the ^{13}C spectrum can be made easily by correlation with the ^1H resonances. Use of the new techniques that use observation of the ^1H rather than the ^{13}C nucleus greatly enhances the sensitivity of ^1H–^{13}C shift correlation and makes it possible to use much smaller sample quantitites than hitherto possible.

Conformational changes in coenzyme B_{12} are universally recognized as being important in B_{12}-dependent enzymatic processes. The solution conformation of coenzyme B_{12} can be determined directly by interpretation of the 2D spin-locked NOE spectrum. A preliminary analysis shows no large conformational differences with the X-ray crystal structure, although some subtle changes can be observed. For other alkyl cobalamins we have found preliminary evidence for more dramatic structural changes. A discussion of these effects, together with a semiquantitative interpretation of the 2D NOE data, will be presented in a future paper.[49]

It has been demonstrated here that some of the newer types of 2D NMR techniques can be of crucial importance to make reliable spectral assignments. As will be demonstrated elsewhere, this new NMR approach provides a powerful new tool for structure elucidation of completely unknown compounds. Although most of the techniques discussed here may be somewhat more difficult than the now well-established COSY, NOESY, and heteronuclear shift correlation experiments, the new methods can provide information previously not available. We therefore expect that the approach outlined here will become widely used in the near future.

Acknowledgment. We thank Rolf Tschudin for continuous technical support, Dr. Laura Lerner for many useful comments during the preparation of the manuscript, and Dr. R. W. K. Lee (U.C.—Riverside) for helpful comments. L.G.M. thanks the NIH for financial support, Grant GM 29225. L.G.M. thanks the NIH for financial support, Grant GM 29225.

Registry No. Coenzyme B_{12}, 13870-90-1.

Supplementary Material Available: HOHAHA spectra showing the ^1H–^1H J-coupled networks, the COSY spectrum, and the downfield ^{13}C region of the ^1H–^{13}C HMQC spectrum (5 pages). Ordering information is given on any current masthead page.

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First Observation of Electroluminescence at the p-Type Semiconductor/Electrolyte Interface Caused by Electron Injection: Energetics of Adsorbed Hydrogen at the p-GaAs Electrode

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Contribution from the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan. *Received February 4, 1986*

Abstract: Electroluminescence (EL) due to a band-to-band transition was observed at the p-GaAs/1 M NaOH and p-GaAs/0.5 M H_2SO_4 interfaces just after the potential was pulsed from the strong negative bias to the potential near the flat band potential. The integrated EL intensity increased with the increase of the cathodic pulse width, i.e., the charge passed during the cathodic pulse, but became constant when the pulse width was longer than ca. 2 ms and the cathodic charge was larger than 350 $\mu C \cdot cm^{-2}$. These results and other evidence suggest that the EL of this system is caused by electron injection from the adsorbed hydrogen atom formed during the cathodic pulse as an intermediate of the hydrogen evolution reaction. The quenching of the EL and the increase of hydrogen evolution reaction rate in the dark by the surface treatment by Ru^{3+} mean that the energy level of adsorbed hydrogen at Ru^{3+} treated p-GaAs is below the conduction band edge at the surface.

The electroluminescence (EL) measurement is proved to be useful for the study of the electrochemical reaction mechanism at semiconductor electrodes,[1] particularly to probe the reaction intermediates[2] and the surface states of semiconductors.[3] EL

Table I. Properties of p-GaAs

sample	dopant	acceptor density/ cm^{-3}	specific resistance/ $\Omega \cdot cm$	mobility/ $cm^2 \cdot V^{-1} \cdot s^{-1}$
1	Zn	1.09×10^{19}	0.0051	64.3
2	Zn	4.66×10^{18}	0.0135	99.1
3	Zn	2.35×10^{18}	0.0236	112.7

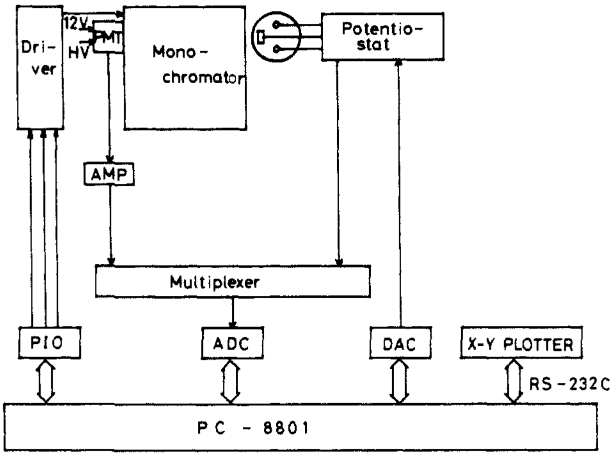

Figure 1. Block diagram for EL measurements.

is usually caused by minority carrier injection under forward bias condition, i.e., hole injection to the valence band of an n-type semiconductor under negative bias and electron injection to the conduction band of a p-type semiconductor under positive bias.[4] There is, however, no report on EL at the p-type semiconductor/electrolyte interface caused by electron injection because p-type semiconductors are unstable and dissolve away under positive bias.[5] Only two types of EL have been reported at p-type semiconductor interfaces. The first report on EL at p-type semiconductor/electrolyte interfaces was by Butler and Ginley.[6] They found EL at the p-GaP electrode, the spectrum of which had a broad band with the peak energy being much smaller than the energy gap of GaP, and proposed that the EL at p-GaP was caused by direct injection of cations into the semiconductor surface. Recently we observed EL due to band-to-band transition at the p-GaAs/$S_2O_8^{2-}$ solution interface under strong negative bias.[7] The result suggests that the EL is caused by *hole* injection, proving the inversion layer formation.

In this paper, we report EL at p-GaAs in aqueous solutions caused by *electron* injection from species generated in situ, most probably adsorbed hydrogen atom, for the first time.

Experimental Section

Materials. p-GaAs single-crystal wafers were obtained from Morgan Semiconductor, Inc., and their properties are summarized in Table I. Ohmic contacts to the crystals were made by using an In–Zn alloy. The electrode surface was etched in HNO_3–HCl (1:1) before each experiment. Reagent grade NaOH and H_2SO_4 obtained from Wako Pure Chemicals Co. Ltd. and water purified by the Milli-Q water purification system (Millipore Corp.) were used to prepare electrolyte solutions. Solutions used for ruthenium treatment were prepared by dissolving 0.026 g of $RuCl_3 \cdot nH_2O$ [Ru content 44–45%), obtained from Mitsuwa Chemicals, Inc., in 10 mL of 0.10 M HNO_3 (Wako Pure Chemicals Co. Ltd.).

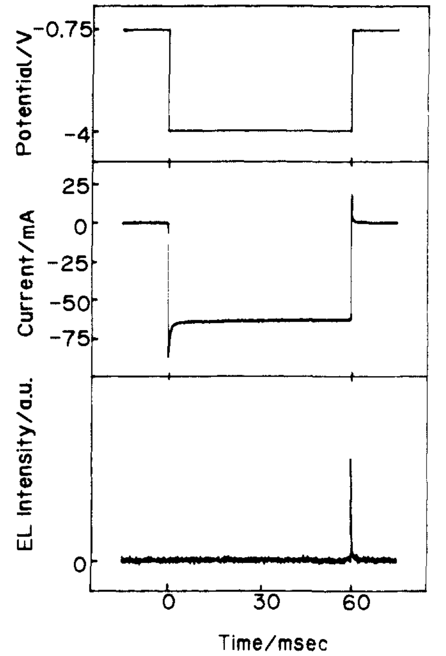

Figure 2. Time sequence of applied potential and resultant current and EL intensity at p-GaAs doped with Zn (2.35×10^{18} cm^{-3}) in 1 M NaOH. EL data were averaged 16 times to improve the signal-to-noise ratio.

Electrochemical and Luminescent Measurements. The block diagram for the measurements is shown in Figure 1. An ordinary two-compartment cell with a flat window was used for all the measurements. The potential of the electrode was controlled by a potentiostat (Hokuto Denko, HA-301) with respect to a Ag/AgCl reference electrode. A large Pt foil which was placed above a GaAs working electrode was used as a counter electrode. The EL intensity was monitored with a photomultiplier (Hamamatsu Photonics Co. Ltd., R1767) which had a response similar to S-1 and was cooled to −20 °C by using an electronic photomultiplier cooler (Hamamatsu Photonics Co. Ltd., C659). A monochromator (Ritsu Oyo Kogaku Co. Ltd., MC-20N), having a grating with 1200 grooves/nm blazed at 0.75 μm, was used to obtain emission spectra. A personal computer (NEC Corp., PC-8801 mkII) was used to provide external potentials to the potentiostat via a 12-bit D/A converter (DAC), to collect the photomultiplier response which was amplified by a fast-response amplifier (NF Electronic Co. Ltd., LI-75A, 1MHz, gain = 100) and the current response via a 12-bit A/D converter (ADC) with an 8 channel multiplexer, and to control the monochromator by sending pulsed signals to a monochromator drive unit (Ritsu Oyo Kogaku, DU-1B) via PIO interface.[8] The main program to set up experimental conditions, etc., was written by using BASIC, but the routine programs to operate DAC and ADC were written by using the machine code to allow fast response and were CALLed from the BASIC program. To improve the signal-to-noise ratio, the signals were averaged 2–100 times. All the data were transferred to and stored on a floppy disk. All the measurements were carried out at room temperature after the solution was deaerated by passing a purified He gas for at least 30 min.

Results

Figure 2 is a typical EL-i-t-relation of p-GaAs (Zn doped, 2.35×10^{18} cm^{-3}) in 1 M NaOH solution when potential was pulsed between −0.75 V (vs. Ag/AgCl) (15 s) and −4 V (60 ms). EL was observed not when the potential was pulsed from −0.75 to −4 V but just after the potential was pulsed from −4 to −0.75 V and diminished very quickly (<10 ms). This result is quite different from the one reported at the p-GaAs/$S_2O_8^{2-}$ interface where EL was observed while the potential was kept at relatively negative potentials (<ca. −2.3 V).[7] Anodic current spike was also observed when the potential was pulsed from −4 to −0.75 V (Figure 2). To study the effect of negative potential pulse limit (V_N) on the EL

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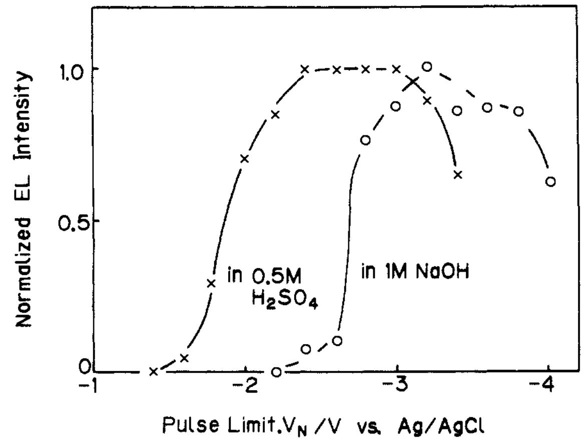

Figure 3. The integrated EL intensity of p-GaAs (Zn: 4.66 × 10^{18} cm^{-3}) in 1 M NaOH (○) and in 0.5 M H_2SO_4 (×) as a function of negative potential pulse limit, V_N. The intensities are normalized to the maximum value in each solution. The positive potential pulse limits were −0.75 V in 1 M NaOH and 0 V in 0.5 M H_2SO_4.

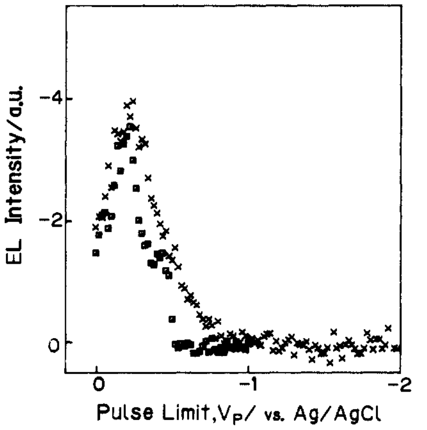

Figure 4. The integrated EL intensity of etched (×) and Ru^{3+} treated (▣) p-GaAs (Zn: 4.66 × 10^{18} cm^{-3}) in 1 M NaOH as a function of positive potential pulse limit, V_p. V_N = 3 V in both cases.

intensities, EL-t relations were measured by changing V_N with a fixed positive potential limit (V_p) as −0.75 V. The EL intensities recorded between 0 and 15 ms (I_{EL}) after the potential was pulsed from V_N to V_p are integrated and are shown in Figure 3 as a function of V_N. The EL was significant when V_N was more negative than ca. −2.5 V. The EL intensity became maximum when V_N was ca. −3.2 V, and it decreased gradually when V_N became more negative. Similar measurements were carried out in 0.5 M H_2SO_4, and V_N dependence of the integrated EL in this solution is also shown in Figure 3. In this case, the positive pulse limit was 0 V. As shown below, since the EL intensity was strongly affected by V_p, the EL intensities were normalized to the maximum value in each solution in order to compare the results in two solutions. The I_{EL}–V_N relation in 0.5 M H_2SO_4 appears more positive than that in 1 M NaOH by ca. 800 mV.

The effect of V_p on the integrated value of EL intensity in 1 M NaOH (V_N = −3 V) is shown in Figure 4. The EL was significant only when V_p was more positive than ca. −0.8 V. The more positive the positive potential limit was, the stronger the EL intensity was. The EL intensity, however, reached a maximum at V_p of −0.2 V and decreased quickly when V_p became more positive than −0.2 V. One must note that the open circuit potential of p-GaAs in 1 M NaOH was ca. −0.7 V, and anodic current due to dissolution of GaAs[9] flowed when the potential became more positive than −0.7 V. The electrode surface after this experiment was very rough, indicating the dissolution of the electrode.

The effect of the time duration for which p-GaAs was kept at V_N on the EL-i-t relation is shown in Figure 5. When the time duration was too short, no EL was observed. The longer the time duration was, the stronger the EL intensity was. The EL intensity, however, became constant when the pulse width was longer than ca. 2 ms. The cathodic charge passed during the negative pulse is also shown in Figure 5 as a function of pulse width.

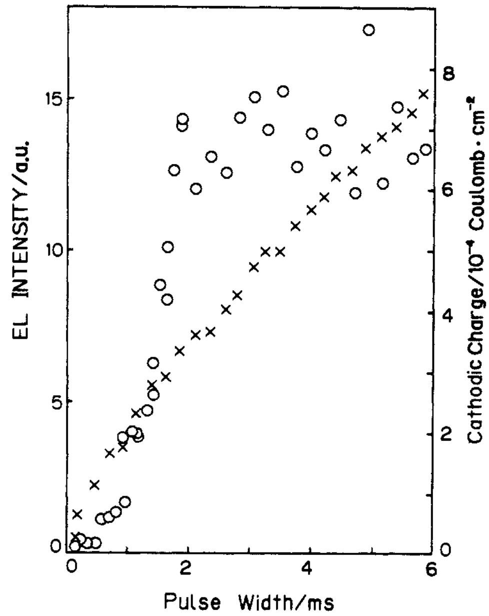

Figure 5. The integrated EL intensity (○) and cathodic charge passed during cathodic pulse (×) of p-GaAs (Zn: 4.66 × 10^{18} cm^{-3}) in 1 M NaOH as a function of pulse width.

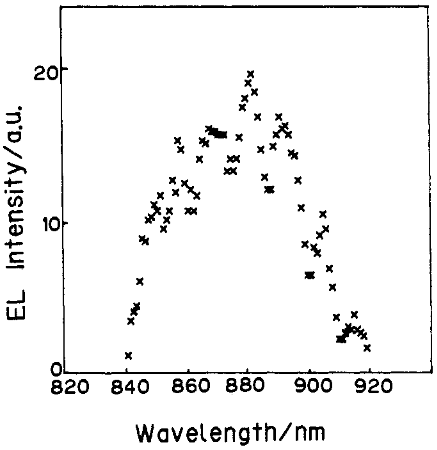

Figure 6. EL spectrum of p-GaAs doped with Zn (4.66 × 10^{18} cm^{-3}) in 1 M NaOH. The potential was pulsed between −0.75 and −4 V. The EL intensity represents the sum of 20 PMT response monitored by A/D converter every 60 μs from the time the potential was pulsed from −4 to −0.75 V. The EL data were averaged for 100 times at each wavelength.

To know the origin of EL, the EL spectrum was obtained and is shown in Figure 6. The peak appeared around 880 nm which is in good agreement with the energy gap of p-GaAs, suggesting that the EL is due to band-to-band transition.[10]

We have already reported that by treating the p-GaAs surface in a solution containing Ru^{3+} ion, the surface state was introduced[11] and hydrogen evolution reaction in the dark was accelerated.[11,12] Thus, the effect of Ru^{3+} treatment on the EL behavior was also studied. As shown in Figure 7, while cathodic current during negative pulse increased, the EL was quenched by the treatment. The original EL behavior was recovered by the etching

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(9) Harvey, W. W. *J. Electrochem. Soc.* **1967**, *114*, 472.

(10) In principle, the comparison between the PL spectrum and the EL spectrum gives the spatial information of the EL generation process. However, the EL intensity of this system was so weak that the slit of the monochromater was wide open with resolution of ca. 5 nm and, therefore, it was not possible to compare the EL spectrum with the PL spectrum in detail.

(11) Uosaki, K.; Kita, H. *Chem. Lett.* **1984**, 953.

(12) Uosaki, K.; Kabe, Y.; Kita, H., unpublished result.

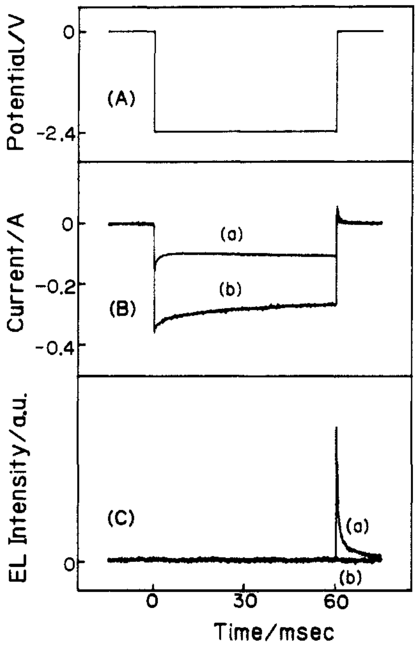

Figure 7. Time sequence of applied potential and resultant current and EL intensity at p-GaAs (Zn: 4.66 × 10^{18} cm^{-3}) in 0.5 M H_2SO_4: (a) etched. (b) Ru^{3+} treated.

treatment. The effect of V_p on I_{EL} of Ru^{3+} treated p-GaAs in 1 M NaOH is also shown in Figure 4. Although no EL was observed when the V_p was more negative than ca. −0.5 V, almost the same values of I_{EL} as those at etched p-GaAs were observed when V_p was more positive than ca. −0.5 V at which anodic dissolution current became significant.

Discussion

The fact that the EL was observed not when the potential was pulsed to negative potential limit but when the potential was pulsed back to positive potential limit (Figure 2) suggests that the mechanism of the EL generation of this system is quite different from that of the p-GAs/$S_2O_8^{2-}$ system[7] and the EL is caused by species generated in situ while p-GaAs was kept at negative potential limit. Since the EL is caused by band-to-band transition (Figure 6), electrons in the conduction band and holes in the valence band are required for the EL generation. When the potential is at the positive limit, the surface concentration of hole which is the majority carrier of p-GaAs is relatively high but that of electron which is the minority carrier of p-GaAs is low. Thus, the fact that the EL was observed at positive potential limit and lasted only less than 10 ms means that the species generated in situ while p-GaAs was kept at negative potential limit injects electron into the conduction band when the potential was pulsed to the positive limit. Some of the electrons injected in this manner recombine radiatively with holes in the valence band. Since the amount of species generated is limited, the EL is only short lived. The energy of reduced species, which can inject electrons into the conduction band when the potential is pulsed to the positive potential limit, must be higher than the bottom of the conduction band *at the surface* when the potential is at the negative potential limit. When the negative potential limit is not negative enough, the reduced species is not generated (Figure 3). When the positive potential limit is not positive enough, the concentration of surface holes in the valence band is not high and EL is not observed (Figure 4). The more positive the positive potential limit is, the higher the surface concentration of holes is and, therefore, the higher the EL intensity should be. However, as shown in Figure 4, the highest EL intensity was observed when the positive potential limit was ca. −0.2 V and the weaker EL was observed when the positive potential limit was more positive than −0.2 V. Since the open circuit voltage of p-GaAs in 1 M NaOH in the dark was ca. −0.7 V, a relatively large anodic dark current was observed at the potentials more positive than ca. −0.2 V where EL started to decline. As mentioned before, the current is due to dissolution of p-GaAs and the electrode surface became very rough after the measurement in Figure 4 was completed. The decline of EL at this potential region should be due to the introduction of the recombination center caused by dissolution of the surface layer.

There are several possibilities for the species responsible for the EL generation. They are adsorbed hydrogen atom (H(a)), which is the intermediate of hydrogen evolution reaction, and Ga, which may be generated by the cathodic decomposition of GaAs and/or H_2O_2 which may be formed by the reduction of residual O_2 in solution even after the deaeration. The fact that EL was observed when the potential was pulsed from the negative limit to the positive limit for very short times excludes the possibility of H_2O_2 or precursor of that as the EL generating species because H_2O_2 (or •OH) generates EL by hole injection[13] and if EL were observed it should be observed while the potential is kept at negative potential limit as was the case at the p-GaAs/$S_2O_8^{2-}$ interface.

Thus, the possible reactions for the EL generation in 1 M NaOH can be written as follows.

At negative pulse limit:

$$H_2O + e_c^- \rightarrow H(a) + OH^- \quad (1)$$

$$GaAs + 3e_c^- + 3H_2O \rightarrow Ga + AsH_3 + 3OH^- \quad (2)$$

At positive pulse limit:

$$H(a) + OH^- \rightarrow H_2O + e_c^- \quad (3)$$

$$Ga + 6OH^- \rightarrow GaO_3^{3-} + 3H_2O + 3e_c^- \quad (4)$$

where e_c^- and p_v^+ are electron in the conduction band and hole in the valence band, respectively. Those in 0.5 M H_2SO_4 can be written similarly as follows.

At negative pulse limit:

$$H^+ + e_c^- \rightarrow H(a) \quad (5)$$

$$GaAs + 3e_c^- + 3H^+ \rightarrow Ga + AsH_3 \quad (6)$$

At positive pulse limit:

$$H(a) \rightarrow H^+ + e_c^- \quad (7)$$

$$Ga \rightarrow Ga^{3+} + 3e_c^- \quad (8)$$

In both solutions, light is emitted by direct recombination of e_c^- and p_v^+ as

$$e_c^- + p_v^+ \rightarrow h\nu \quad (9)$$

The pH dependence of I_{EL}–V_N relations supports both species i.e., H(a) and Ga, as the electron injecting species.

Since only species generated under cathodic bias in situ can inject electron into the conduction band and generate the EL, the EL declines as the species is consumed and I_{EL} is correlated with the amount of electron injecting species or the charge passed during cathodic pulse. The result in Figure 5 shows that only a certain amount of electron injecting species can be formed. It is quite interesting to note that I_{EL} reached a constant value when the charge at the cathodic pulse reached ca. 350 $\mu C{\cdot}cm^{-2}$ which is equivalent to about a monolayer of species, if one assumes that the roughness factor of the electrode was 1.5, all the charges were used to generate the electron injecting species and the generation reaction is a one-electron process. There is no reason to stop at the monolayer in the case of Ga formation (reaction 2).[14] Indium formation by the cathodic decomposition reaction of p-InP under illumination proceeds even more than 50 monolayers.[15] Fur-

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[13] Gerischer, H.; Müller, N.; Haas, O. *J. Electroanal. Chem.* **1981**, *119*, 41.

[14] Actually, since reaction 2 is a three-electron process, the surface coverage in this case is about half a monolayer even if one assumes the roughness factor of the electrode is 1.

[15] Uosaki, K.; Kita, H. *Sol. Energy Mater.* **1983**, *7*, 421.

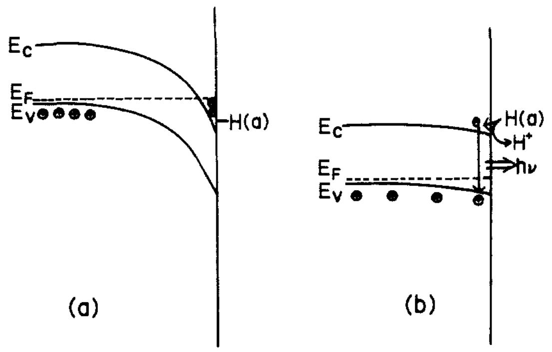

Figure 8. Proposed model for the EL caused by electron injection: (a) under strong cathodic bias; (b) near the flat band potential.

thermore, Auger Electron Spectroscopic measurements of the n-GaAs electrode on which hydrogen evolution reaction took place for 30 min at −1.5 V (current density = ca. 1 Å·cm^{-2}) provided evidence of no enrichment of Ga at the surface region.[16] In addition, there is no possibility that the amount of adsorbed hydrogen exceeds one monolayer. Therefore, with all the evidence presented above, we propose that the most probable species responsible for the EL generation is the adsorbed hydrogen atom. The model which explains the EL generation is shown in Figure 8. Thus, H(a), the energy of which is higher than that of the bottom of the conduction band *at the surface*, is generated when p-GaAs is kept under strong negative bias (reaction 1 or 5) and injects electron into the conduction band (reaction 3 or 7) when the potential is pulsed to the positive potential limit which is close to the flat band potential. Some of the injected electrons recombine radiatively with holes in the valence band (reaction 9) which is the majority carrier of p-GaAs. The results of Ru^{3+} treated p-GaAs can also be explained by this mechanism. Thus, the energy level of H(a) at the Ru^{3+} treated p-GaAs surface should be within the energy gap and, therefore, no EL should be observed.[17] The increase of dark hydrogen evolution current is caused by the lowering of the H(a) energy level as proposed by Bard for the effect of Pt on the photoelectrochemical hydrogen evolution reaction.[18]

Acknowledgment. Prof. A. B. Ellis and Dr. W. S. Hobson are acknowledged for the donation of p-GaAs single crystals. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

Registry No. GaAs, 1303-00-0; H, 12385-13-6; H_2, 1333-74-0; Ru^{3+}, 22541-88-4; $RuCl_3$, 10049-08-8.

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(16) Kaneko, S.; Uosaki, K.; Kita, H., unpublished result.

(17) There may be a possibility of sub-band emission in this case. Our detection system, however, can measure the emission only up to 1100 nm and no sub-band gap EL was detected within this region.

(18) Bard, A. J. *J. Phys. Chem.* **1982**, *86*, 172.

Topologically Determined Charge Distributions and the Chemistry of Some Cage-Type Structures Related to Adamantane

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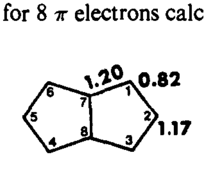
Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received July 29, 1985*

Abstract: The rule of topological charge stabilization says that nature prefers to locate heteroatoms at those positions in a molecular structure where connectivity and electron filling level tend to accumulate or deplete electron density in an isoelectronic, isostructural, homoatomic system. The rule can be rationalized on the basis of first-order perturbation theory. Here we apply the rule to some cage-type structures related to adamantane. Examples include P_4S_3, P_4S_4, P_4S_5, and P_4S_6, as well as many others. Extended Hückel calculations of Mulliken atom populations in homoatomic systems correlate with the positions of atoms of different electronegativities in these structures. Topologically determined charge distributions can explain some of the chemistry of these systems.

A recent survey of planar conjugated molecules has demonstrated that connectivity and the number of electrons occupying the molecular orbital system determine the patterns of charge densities in homoatomic systems.[1] The *rule of topological charge stabilization* says that nature prefers to locate heteroatoms at those positions where connectivity and electron filling level tend to accumulate or deplete electron density. An example from planar conjugated molecules is pentalene (1) shown with charge densities for 8 π electrons calculated by the simple Hückel method. Charge densities at positions 1, 3, 4, and 6 are considerably smaller than those at the other sites. The rule of topological charge stabilization says that less electronegative atoms would be favored in those positions with low charge density. Pentalene is known only as the heavily substituted 1,3,5-tri-*tert*-butyl derivative,[2] but the isoelectronic inorganic analogs (2, 3) have been prepared.[3,4] In 2 and 3 borons are located at positions 1, 3, 4, and 6, and more electronegative nitrogens or sulfurs occupy the other sites, arrangements in which the electronegativities of the constituent atoms match the distribution of charge densities determined by connectivity in 1, the homoatomic, isoelectronic structure which we refer to as the *uniform reference frame*. That the pattern of charge densities is also a function of the number of valence electrons can be seen by comparing the charges for the pentalene dianion (4, 10 π electrons) with those of pentalene itself (1). In



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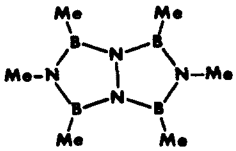

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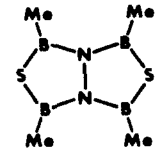

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