Charge Transfer Process at Illuminated Semiconductor/ Electrolyte Junctions Modified by Electrodeposition of Microscopic Metal Grain

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ABSTRACT

Layers made of microscopic Pt grains, optically transparent, with various morphologies are deposited on n-GaAs by electrocrystallization. It is shown that the modified GaAs photoanode is long-term stabilized under illumination in aqueous electrolytes provided that the film presents some required structural properties, *e.g.*, size and density of Pt nuclei. In fact, correlations between the film morphology [studied by transmission electron microscopy (TEM)] and the stabilization of the modified electrode [studied by I-V, C-V measurements and the rotating ring-disk electrode (RRDE) technique] are observed. The mechanism of stabilization by Pt grains is also investigated by considering the surface state distributions, determined by photocapacitance experiments, at both bare and modified interfaces.

The use of n-type narrow bandgap semiconductor/electrolyte (SC/EL) junctions as practical photoelectrochemical (PEC) solar cells is still hampered by the degradation of the photoanode, *i.e.*, the photocorrosion and the chemical attack of the semiconductor. Many years ago photoanodes (Si, GaAs, GaP...) were reported to be effectively protected by vacuum deposition of thin metal layers (1-4), but with some disadvantages: (i) a too large film absorption and (ii) the fact that the modified interface behaves like a semiconductor/metal Schottky barrier dipped in a liquid. Recently the concept of discontinuous metal films makes metal deposition more attractive because such films can be optically transparent (5) and the intrinsic properties of the SC/EL contact (e.g., photovoltage) can be preserved (6). At present discontinuous metal films proved to be suitable for catalyzing the hydrogen photoevolution at p-InP and p-Si (7, 8) and for stabilizing n-Si and n-GaAs in aqueous media (9, 10). Reference (9) puts forward a theory to interpret the spectacular photovoltage of n-Si electrodes modified with a discontinuous metallic film. As the Si metal-free surface is passivated in aqueous media the Pt grains act as the only pathway through the oxide so the invoked catalytic effect is not clear. Considering the above question the present paper intends to bring a better understanding of the role played by the Pt grains. For that purpose we must (i) consider a semiconductor which does not passivate and (ii) be able to vary easily the morphology (density, size of the grains, distribution) of the deposited film. The second point is essential because according to Ref. (9), we expect correlations between the photoelectrochemical behavior of the modified interface (I-V, stabilization . . .) and the film morphology.

The present study deals with the n-GaAs/aqueous electrolyte junction modified by electrodeposition of Pt because GaAs does not passivate in water solution (unless the pH is close to 7); furthermore a previous work in our laboratory suggests that the use of electrocrystallization of Pt on n-GaAs should fulfill the second above requirement because the nucleation and growth modes of the film proved to be easily changed by just modifying some parameters of the electrodeposition (11). The charge transfer at such compound electrodes is discussed through (i) the observed correlations between the film morphology and the stability of the electrode and (ii) electrical characterizations of the interface. By choosing a relevant electrolyte our results show that n-GaAs can be very well stabilized in aqueous solution by electrodeposition of microscopic Pt grains.

Experimental

Electrodes.—Photoanodes are made of n-GaAs $(2 \cdot 10^{16} \text{ cm}^{-3}; (100)$ orientation) single crystals purchased from MCP, Limited. After a mechanical polishing with a 1 μ m diamond paste, the surface is chemically etched with a

 (H_2SO_4, H_2O_2, H_2O) (2, 2, 25 volume) mixture of 1 mn, rinsed with 18 M Ω H₂O, dipped in a 0.1% bromide-methanol solution for 1 mn and finally H₂O rinsed and blown dried with argon.

Electrical and electrochemical characterizations.-All measurements are performed in a potentiostatic mode in a three-electrode electrochemical cell. All potentials refer to the saturated calomel electrode (SCE). Illumination is provided by a 100W quartz halogen lamp; the intensity is changed by means of neutral density filters. Impedance measurements are performed with a 1174 Solartron frequency response analyzer operating at 25 kHz. The Mott-Schottky plots (C^{-2} -V), readily obtained through the classical RC parallel analysis of the data (12), give the band position in the dark ($V_{\rm FB}$) and under illumination ($V_{\rm FB}^*$). The surface state distribution is determined by the photocapacitance technique which consists in measuring the variations of the space charge capacitance of the semiconductor as a function of the incident subgap photon flux; for more details about the technique itself and the spectrum analysis one should refer to Ref. (13, 14a). The stabilization ratio S of the interface is measured with a rotating ring-disk electrode (RRDE). S is defined as the ratio between the photocurrent associated with the oxidation of the redox species over the total photocurrent. The photocurrent I_{pH} generated at the 6 mm diam n-GaAs disk leads to a photo-oxidation of redox species which amount is detected with the Pt ring (external and internal diam 8.8 and 7.2 mm, respectively) with a collection factor N = 0.32in close agreement with its calculated value: then $S = I_r$ NI_{pH} , where I_r is the ring current. In the following, we only show results obtained in I^-/I_3^- solutions acidified with H_2SO_4 : the polarization of the disk is +0.5 V/SCE (i.e., in the region of photocurrent saturation), that of the ring is -0.2 V/SCE (i.e., in the diffusion plateau of the reduction reaction).

Surface characterization.—The interfacial composition is analyzed with the 2 MeV Van der Graff accelerator of the Groupe de Physique des Solides de l'ENS. The number of deposited Pt atoms/cm² is measured with a 2 MeV ⁴He⁺ beam normally incident; the amount of oxygen atoms is determined by using the ¹⁶O(d, p) ¹⁷O* nuclear reaction at $E_n = 850 \text{ keV}$ (15).

 $E_{\rm p}=850~{\rm keV}$ (15). The morphology and the structure of deposited films are studied by transmission electrode microscopy (TEM) and transmission electron diffraction (TED). Samples are prepared with the extractive replica technique (11).

Pt electrodeposition.—Pt coating is performed by electrocrystallization of Pt on n-GaAs from a $(NH_4)_2$ PtCl₆ solution either at pH = 0 or 3.3. Just after etching the rotating disk electrode is dipped in the plating solution at 0 V/SCE and a negative pulse of potential V_d is applied. At present

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the main point of the technique consists in its ability to produce very different film morphologies. For example the TEM observations of Fig. 1a and 1b show that the grain density is strongly dependent on the potential of deposition V_d at pH = 0 while there size is ≈ 2.4 nm; for a given V_d the size of the grains depends on the time of deposition t_d . Figure 1c evidences the influence of the pH: at pH = 3.3the grains are much larger (20 nm) and less numerous than at pH = 0. The interpretation of these results is out of the scope of this study and will be published elsewhere (16). As a final remark, TED patterns present dotted rings in agreement with crystallized Pt grains without preferential orientations (11).

Results

Figure 2 presents TEM observations of two different surfaces of GaAs after the same PEC test: each electrode is kept under illumination in a 7*M* NaI (pH = 0) solution for 30 mn ($I_{pH} = 0.3 \text{ mA/cm}^2$; V = +0.5 V/SCE). These observations clearly demonstrate that the naked electrode (Fig. 2a)



Fig. 1. TEM observations of electrodeposited Pt films on n-GaAs. (a, top left) $V_d = -0.5V$, and (b, above) -0.85V at pH = 0; (c, left) $V_d = -0.7V$ at pH = 3.3.

is much more disturbed by corrosion pits than the Ptcoated one (Fig. 2b). The small dots (4 nm) in Fig. 2b are the Pt grains. These corrosion pits proved to be mainly due to the chemical attack at the surface by the solution because they are observed (with almost the same size) when the electrode is only kept in the dark for the same time. This agrees with the observed chemical etching of GaAs in solutions containing iodine (17). Therefore Fig. 2 indicates that (*i*) the Pt film stabilizes the electrode against the chemical attack and (*ii*) the photocorrosion, if it exists, occurs with no preferential site. This is why we directly determined the stabilization ratio S of the electrode with our RRDE which GaAs disk has been Pt coated prior to measurement.

Figure 3 evidences the ability of our Pt films to protect n-GaAs under illumination. We report here the variations of the bandedge displacement $\Delta V = V_{\rm FB}^* - V_{\rm FB}$ under illumination as a function of the stabilization ratio *S* for increasing times t_d of Pt electrodeposition ($V_d = -0.7$ V/SCE). In the 1*M* NaI + 0.5*M* H₂SO₄ solution [denoted 1*M*]



Fig. 2. TEM observations of n-GaAs surfaces after the same PEC test (see text). (a, left) Naked surface; (b, right) Pt-coated surface $(V_d = -0.85V; t_d = 2s \text{ at } pH = 0)$.



Fig. 3. Variations of the shift $\Delta V = V_{FB}^* - V_{FB}$ vs. the stabilization ratio S for Pt-coated n-GaAs electrodes in 7M (\bigcirc) and 1M(\bigcirc) Nal solutions with increasing times of deposition t_d of Pt (potential of deposition $V_d = -0.7V$).

NaI (pH = 0) in the following], the stability obviously increases with the amount of deposited Pt: S is only 0.74 for a naked surface and becomes 0.97 for $t_{\rm d}$ = 10s (*i.e.* $\simeq 10^{16}$ Pt atom/cm²). In the 7M NaI (pH = 0) solution [the pH is adjusted with H_2SO_4 as in Ref. (18)], the sensitivity of the RRDE technique is not able to detect any improvement of S because it is initially >0.99 (18). Figure 3 also shows that ΔV decreases in 1M NaI while S increases. Such a result is quite similar to that observed with bare n-GaAs photoanodes in contact with variously stabilizing redox couples (19). Reference (19) demonstrates that ΔV is connected with the remaining photocorrosion of the electrode: the smaller the ΔV , the smaller the photocorrosion. According to Fig. 3 this result applies with Pt-coated electrodes; therefore in the following we will consider, in a given medium, that measuring ΔV is a practical way to estimate the stability of the electrode. The goal is to obtain the smallest possible ΔV with the smallest possible film absorption $(\Delta V = 0 \text{ means } S = 1.0).$

As a first conclusion it appears that our electrodeposited Pt films effectively stabilize the surface of GaAs against both the chemical corrosion (Fig. 2) and the photocorrosion (Fig. 3). But the question arises: how do such microscopic grains act? Indeed they only cover a few percents of the whole surface.

To answer the above question we have produced a large variety of film morphologies and tested the resulting interfaces. The test consisted in keeping, as in Fig. 2, the electrode under illumination in 7M NaI ($I_{pH} = 0.3$ mA/cm²; V = +0.5 V/SCE) for 30 mn. The interface was then characterized by the measured shift ΔV of the bandedges, *i.e.*, its stability. The surface was also observed by TEM, as shown in Fig. 2b, and has been characterized by (i) the corrosion pit coverage θ_{corr} (which accounts for the chemical attack), (*ii*) the Pt coverage θ_{Pt} , (*iii*) the grain density N_o (cm⁻²), and (iv) their diameter d (nm). We checked that the values of $N_{\rm o}$ and d were consistent with the amount of deposited metal atom/cm² (measured by RBS) by considering hemispherical Pt grains. The photoelectrochemical (PEC) test were performed in the 7M NaI solution because our aim was to long-term stabilize the surface and it seemed more relevant to begin with a good enough stabilizing medium.

The main correlations between the film morphology and the stability against both corrosion and photocorrosion are reported in Fig. 4 and 5, respectively. These figures show that both θ_{corr} and ΔV decrease for Pt coverages as low as 10^{-3} : $\theta_{corr} = 0.25$ and $\Delta V = 120$ mV for naked electrodes within the same conditions. This already indicates that Pt does not act as a simple mask. Until $\theta_{Pt} = 0.2$ the reduction of both ΔV and θ_{corr} is rather slow. For $\theta_{Pt} > 0.2$ the faster variations of θ_{corr} and ΔV suggest that 0.2 is a critical Pt coverage to reach the stability. However, it seems that the results depend on the film morphology especially for ΔV (Fig. 5a). For example, deposits with small densities N_0



Fig. 4. Variations of the corrosion pit coverage θ_{corr} after the PEC test as a function of θ_{Pt} (a) and the Pt grain density N_o (b). The 2 (\bullet) and 4 nm (\blacktriangle) grains are obtained at pH = 0. $\theta_{corr} = 0.25$ for a naked surface (see text for the description of the photoelectrochemical test).

 $(\simeq 10^{10} \text{cm}^{-2})$ and large grains $(d \simeq 30 \text{ nm})$, obtained at pH = 3.3 (\Box), are less efficient than those obtained at pH = 0 with larger N_{o} even if the nuclei are much smaller ($\simeq 2.4 \text{ nm}$)



Fig. 5. Variations of the shift ΔV after the PEC test as a function of θ_{Pt} (a) and the Pt grain density N_a (b). The 20-40 nm diam grains ([]) are obtained at pH = 3.3. The others [2 (\bullet) and 4 nm (\blacktriangle)] are obtained at pH = 0. $\Delta V = 120$ mV for a bare surface. The bandedge shift ΔV is measured for a light intensity corresponding to a photocurrent of 0.3 mA/cm² (see text).

(Fig. 5b). This means that N_o is the prevailing parameter in the morphology for a given Pt coverage. Note that we cannot ascertain whether grains smaller than 4 nm but with a density larger than $5 \cdot 10^{12}$ cm⁻² are more efficient. At the present time it seems that $2 \cdot 10^{12}$ cm⁻² nuclei is a critical density; the corresponding optimum grain size is 4 nm. So far it appears that deposits performed at pH = 3.3 must be ruled out because of a too small N_o . Nevertheless, even if N_o was greater, that kind of film would not be interesting because of a too large light absorption.

Figure 6 presents the steady-state current-voltage characteristics under illumination of a rotating disk n-GaAs electrode in contact with a 7M NaI (pH = 0) solution: curve a corresponds to the bare surface and curve b to the Ptcoated one (potential of deposition -0.7V, time of deposition 10s). The film presents a morphology ($N_o = 2.6 \ 10^{12}$ cm^{-2} , grain size ~4 nm) close to the optimum. As a first conclusion the film is found to be optically transparent because the illumination level has been kept the same for both naked and modified interfaces. The band position (pulled out from C^{-2} -V Mott-Schottky plots) in the dark is almost unaffected by the presence of Pt at the surface. On the contrary, the downward shift of the bandedges under illumination is markedly reduced at the Pt-coated electrodes $[\Delta V(b) = 0.08V]$ with respect to that of the naked surface $[\Delta V(a) = 0.25V]$. According to Fig. 5 this means that the stability is increased; note that ΔV is smaller in Fig. 5 because of a weaker illumination. Finally, the gain in photovoltage (0.05V) should not be ascribed to an increase of the hole transfer kinetics if one considers the respective positions of the bandedges under illumination (right arrows) and that of the onset potentials. Indeed it is well known that the closer to $V_{\rm FB}$ ^{*} the onset potential, the faster the transfer (20).

In order to explain how the stability of the surface can be improved without any significant increase of the transfer kinetics we have performed capacitance and photocapacitance measurements to determine, respectively, the potential distribution and the surface state distribution at the interface. For thick electrodeposited Pt layers the flatband potential at the n-GaAs/Pt solid contact is -0.96V with respect to Pt. This value corresponds almost to the barrier height measured at the bare n-GaAs/7M NaI (pH = 0) junction ($V_{\rm FB} = -0.82$ V/SCE; $V_{\rm redox} = +0.10$ V/SCE). This explains that Pt does not affect the band position of GaAs in iodide solutions. On the contrary, as soon as the electrode



Fig. 6. I-V characteristics of the n-GaAs/7M Nal (pH=0) contact. a, Bare electrode; b, Pt-coated electrode ($V_d = -0.7V$; $t_d = 10s$ at pH=0). The band position in the dark V_{FB} (left arrows) shifts positively towards V_{FB}^* (right arrows) under illumination by an amount of $\Delta V(a)$ and $\Delta V(b)$, respectively. The illumination level is the same for both interfaces.



Fig. 7. Photocapacitance spectra of a bare n-GaAs surface in contact with 7M Na1. (a) Single beam experiment; (b) with superimposed interband illumination ($I_{p\rm H} = 2~\mu$ A/cm²).

is illuminated in 7M NaI the SC bandedges move down at the naked surface (see Fig. 3) whereas they remain unchanged when it is completely covered with Pt. Figures 7 and 8 present the photocapacitance (PC) spectra of both a bare and a Pt-coated electrode within single beam (Fig. 7a, 8a) and dual beam experiments (Fig. 7b, 8b). We recall that in a single beam experiment the electrode is only subgap illuminated; in a dual beam experiment a weak interband



Fig. 8. Same as Fig. 7 but for a Pt-coated electrode ($V_d = -0.7V$; $t_d = 4s$ at pH=0). (a) Single-beam experiment; (b) with superimposed interband illumination ($I_{pH} = 2 \mu A/cm^2$).

illumination ($I_{pH} = 2 \mu A/cm^2$) is superimposed. The band bending is 0.95V in all experiments; $C_0 = 14.60 \text{ nF}$. All the spectra are normalized with respect the incident subgap flux at 1.35 eV (10^{16} cm⁻²s⁻¹). The electrode area is 0.3 cm². Considering the single-beam experiments (Fig. 7a and 8a) one sees that the spectra present the same general shape with the same transitions except for the small peak around 1.27 eV when the electrode is coated with Pt. This means that (i) the peak is related to surface states and (ii) it is induced by the interactions between Pt and the GaAs surface. The other common transitions have been identified elsewhere: the main peak at 0.85 eV is related to the wellknown bulk state EL2 in GaAs (14a), the transitions at 1.0V and 1.15 eV are related to the corrosion intermediate states and the transition at 1.32 eV accounts for the surface bonds (14b). From one spectrum to another differences also appear as far as the quantities δ_i , amplitude in ΔC between two consecutive transitions, are concerned. Both δ_1 and δ_2 are smaller for the Pt-modified surface. This is even more pronounced when the interband illumination is added (Fig. 7b and 8b). When the electrode is Pt treated the amplitudes δ_1 and δ_2 remain unchanged whereas they become smaller for a naked electrode. On the contrary, the decrease in the EL2 peak is common because it is a bulk state. At last note that the Pt-related peak is still present in such a dual beam experiment (Fig. 8b).

Discussion

This section is intended to give an interpretation for (i) the stabilizing effect of a transparent Pt film and (ii) the observed correlations between the stability of the surface and the film morphology.

The small peak around 1.27 eV in the photocapacitance spectra of Fig. 8 accounts for the presence of two surface states (14) induced by Pt: $E_1 = E_C -1.25$ eV and $E_2 = E_C -0.15$ eV. This result is quite consistent with the position of the Fermi level at the surface of GaAs covered with submonolayers of various metals (21). Figure 9 gives only the state distribution at the interface. The corrosion states ($E_C -1.0$ eV and $E_C -1.15$ eV) are still present because the Pt film is discontinuous.

The quantity δ_1 (δ_2) (Fig. 7 and 8) is related to the number of available optical transitions between the state $E_{\rm C} - 1.0 \text{ eV}$ ($E_{\rm C} - 1.15 \text{ eV}$) and the conduction band (CB); that is to say it accounts for the state density and/or the state population in the corresponding state. In the dark (single-beam experiment) the smaller values of δ_i in presence of Pt suggest that there are less corrosion defects at the surface. This result is consistent with our previous interpretation of these defects which were regarded as oneelectron surface bonds (19); Pt ad-atoms are in fact likely to bring the missing electron and create a much stronger chemical bond as is proved by the position of both states E_1 and E_2 (they are close to the SC bands). When electronhole pairs are photogenerated (dual beam experiment), the population in the corrosion state depends on the surface. For the naked surface (Fig. 7b) δ_1 and δ_2 become smaller. This behavior is attributed to a hole trapping process in the corrosion states at the illuminated n-GaAs electrode (13, 14b). As a matter of fact, at a naked surface holes are transferred to solution at the top of the valence band (VB) (redox reaction, i.e., stabilization process) and through the corrosion intermediates (photocorrosion process) as it is depicted in Fig. 10a (19); δ_1 and δ_2 decrease in Fig. 17b because of a net hole population in the corrosion states. On the contrary, when the electrode is Pt coated (Fig. 8), holes do not transmit anymore through the corrosion states because δ_1 and δ_2 are unchanged (Fig. 8b) in agreement with the better observed stability. This means that they are no longer transferred to solution through the metal-free interface because both pathways in Fig. 10a are spatially coupled. They must therefore be transferred via the very Pt grains (where no corrosion occurs); the state E_1 (spatially located at the grains) is likely to favor this mechanism because of its energy localization in the bandgap (Fig. 9). However we cannot say, at present, whether the transfer occurs at the state E_1 or at the top of the VB at the local Pt/GaAs contacts (Fig. 10b).

The schematic band diagram of the interface under illumination is depicted in Fig. 11; it comes from our capacitance measurements (see previous section). In the dark, no band modulation occurs at the surface because the band positions of the semiconductor are the same even if it is completely covered with Pt. On the contrary under illumination the metal free surface undergoes a downward shift of the bandedges of GaAs and a band modulation appears: $E_{\rm C}({\rm M}) - E_{\rm C}({\rm S}) = 0.12$ -0.25 eV depends on the illumination level. Figure 11 immediately suggests that a photogenerated hole close to the surface is likely to be



Fig. 9. Interface state distribution at a n-GaAs/Pt/7M Nal (pH=0) contact. $E_1 = E_c - 1.25$ eV and $E_2 = E_c - 0.15$ eV are the Pt-induced states.



Fig. 10. Schematic transfer process at an illuminated n-GaAs/7M. Nal (pH=0) contact when the electrode is bare (a) or Pt coated (b). For the naked surface both the direct transfer, at the top of the valence band ($\underline{1}$; redox reaction), and the indirect one, through the corrosion states ($\underline{2}$; photocorrosion) are spatially coupled. For the sake of simplicity only one corrosion state is figured. In presence of Pt the holes transit spatially at the Pt grains either directly ($\underline{1}$) or indirectly ($\underline{2}$ ' through the state E_1 .



Fig. 11. Schematic energy band diagram of the illuminated contact of Fig. 6. $E_{\rm C}(M)$ - $E_{\rm F}(M)$ is the barrier height at the Pt/GaAs solid contact. E_1 is the Pt-induced state. $E_{\rm C}$ (S) and $E_{\rm V}$ (S) $[E_{\rm C}(M)$ and $E_{\rm V}(M)]$ are the band positions at the metal-free (covered) surface.

caught by a Pt grain because the energy diagram favors it. This remark will be of importance in the following discussion.

Any photogenerated hole that reaches the space charge layer is driven by the electric field towards the interface: this latter fact, according to Ref. (25), does not present any lateral component even in the case of Fig. 11. Therefore the mean trajectory of the hole is normal to the surface although it actually presents a much more complex trajectory due to collisions (22). The time between two collisions is $\tau_t = \mu_p m_p^*/q$ where μ_p is the hole mobility, m_p^* the effective mass of the hole, and q the electronic charge (23). For GaAs, $\mu_p = 0.04 \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$, $m_p^* = 0.45 m_o (m_o \text{ is the mass of})$ an electron at rest) (23), lead to $\tau_t = 10^{-13}$ s: this corresponds to a distance between two collisions $\lambda_t = 10 \text{ nm} (\lambda_t^2 = D_p \tau_t)$ with $D_p = 10 \text{ cm}^2\text{s}^{-1}$ for holes in GaAs). It must be then considered that the hole also randomly moves parallel to the surface and particularly just below it: this hazardous trajectory must not extend over more than a few λ_t with respect to its original trajectory towards the interface. Moreover, knowing that the rate constants at the local metal/SC and electrolyte/SC contacts are, respectively, 10⁷ cm/s (22) and 5 \times 10 3 cm/s (19), one finds that a hole needs $\tau_1 = 10^{-14} s$ and $\tau_2 = 10^{-11}$ s to cross the respective interfaces. This means that every hole arriving at the metal-free surface undergoes a great number of collisions in the vicinity of the surface because (i) $\tau_t \ll \tau_2$ and (ii) $\tau_t \ll \tau_p$, the lifetime of holes in GaAs. Therefore, while randomly moving along the surface (over λ_t), around a mean position, this very same hole can encounter a Pt grain on which it will transit towards solution, without corroding the surface, because (*i*) of the band modulation (see Fig. 11) and (*ii*) $\tau_t \simeq \tau_1$. With such simple considerations, it is now obvious that the probability for a hole to encounter a metal grain, i.e., the stability, depends on their density N_o , in agreement with Fig. 5.

So far it turns out that the interpretation we give for the PC spectra (Fig. 7 and 8) agrees fairly well with that pulled out from the considerations of the band modulation (Fig. 11) and the various transit times (see above). The stability comes from a hole transfer through the Pt grains although they cover only 20% of the whole surface. Note that the state E_1 is likely to reinforce the band modulation; in the same way increasing the light intensity is not too unfavorable because it should increase $E_C(M) - E_C(S)$ (Fig. 11). At last it seems that the transfer kinetics at the Pt/solution interface is not critical provided that it is not slower than that found at the SC/solution contact. In our case these two kinetics must be nearly the same because both a naked or a completely covered surface present the same photocurrent-voltage characteristics under illumination (in the sec

ond case the kinetics at the SC/metal contact is not the limiting step). This reconciles the better stability with an apparently unaffected macroscopic kinetics (Fig. 6). As a matter of fact the above discussion, strictly speaking, rules out a catalytic effect of the Pt grains: they act only as an intermediate pathway.

Until now we have only dealt with the protection against the photocorrosion, *i.e.*, when holes are injected at the surface from the bulk of the illuminated SC. Knowing that a chemical attack is a hole injection from oxidizing species in solution (24), it seems realistic to think that the stabilizing process is the same in that case if we consider Fig. 4 and 5.

The magnitude of the relaxation time τ_t for holes and its associated length $\lambda_t = 10$ nm should lead to a critical value of the nucleus density of $5\cdot 10^{11}~{\rm cm^{-2}}$ in the case of perfectly well-distributed grains. Indeed in that case holes would have a large probability of encountering a metal grain and then being transferred to solution through it (see above); therefore S should be unity (*i.e.*, $\Delta V = 0$). The experimental critical value of N_0 is somewhat greater $(2 \cdot 10^{12} \,\mathrm{cm}^{-2})$ because our deposited grains are not homogeneously distributed at pH = 0 (Fig. 2b). At pH = 3.3 (Fig. 1c) the nucleus distribution is better but N_{\circ} is too small (< $6 \cdot 10^{10}$ cm⁻²). According to these statements it seems that greater N_0 , even with smaller Pt grains, would be even more favorable for stabilizing the electrode. However the role played by the size of the grains is not completely clear. One can understand that if they are smaller than 1 nm the band modulation is attenuated because the energy levels at the local SC/metal contacts are quantized (9). For 2 nm diam grains this is no more true. The difference in stability observed with 2 and 4 nm grains must arise either from the coverage θ_{Pt} , *i.e.*, the probability to meet a grain, at a given density (Fig. 5b) or a decrease in the tunneling probability through the well, for holes, due to Pt (Fig. 11). Therefore the optimum film morphology we give $(N_0 > 10^{12} \text{ cm}^{-2}; d \approx 4 \text{ nm})$ is explained by simple consideration.

The above-mentioned results imply several remarks: as λ_t is an intrinsic property of the SC the critical density N_o should depend on the chosen material and its doping level (23). In the same way, for a given SC, the nature of the deposited metal should play only through the amplitude of the band modulation. Further work in that field seems very interesting for the understanding of our model.

Notice that, as in the work of Nakato *et al.* (9), Fig. 6 shows that our modified interface presents a greater opencircuit voltage ($V_{oc} = 0.53V$) than that obtained with a naked surface or completely covered surface (*i.e.*, Schottky barrier); $V_{oc} = 0.48V$ in both latter cases. This result has been obtained without passivation of the metal-free interface. Preliminary results with 7M NaI (pH = 7) show that $V_{oc} = 0.6V$ with stable photocurrents can be obtained with the deposit of Fig. 6; on the contrary, in the same conditions, a naked electrode passivates in a few minutes; before this, the transient V_{oc} is still 0.48V. This means that a new interface has been created with different properties. Such a result can be interpreted within the framework of the theory developed by Nakato *et al.* (25) assuming that the field distribution is the same when $E_C(M)$ lies above E_C (S).

Before concluding, we want to stress that this work deals with the long-term stability of GaAs. In 7*M* NaI-(*p*H = 0) the remaining corrosion is initially 10⁻³ of the total photocurrent for a naked surface (18). According to Fig. 3 we can assume, as a first approximation, that 1-*S* and ΔV are proportional; the coefficient depending obviously on the medium at a given photon flux. This means that the lifetime of the electrode (b of Fig. 6) is at least one year, *i.e.*, three times greater than that of the naked electrode (0.5 mm thick) under strong illumination (18 μ A/cm²) because $\Delta V(\alpha)/\Delta V(b) \approx 3$.

Conclusions

The present work shows that n-GaAs photoanodes can be very well stabilized in aqueous electrolytes by electrodeposition of microscopic metal grains. The film morphology appears to be the key parameter to effectively protect the surface against both the chemical etching and the photocorrosion. Even for small Pt coverages (10-20%) most of the holes transit towards solution via the very Pt grains, provided that their density $N_o > 10^{12}$ cm⁻², because of surface diffusion. No marked improvement of the transfer kinetics is detected. Such modified electrodes prove to be of interest because their photovoltaic properties are better than those of a naked electrode or those of a solid Schottky barrier.

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Semiconductor Electrodes, 62. Photoluminescence and Electroluminescence from Manganese-Doped ZnS and CVD ZnS Electrodes

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ABSTRACT

The photoluminescence (PL) and electroluminescence (EL) from single-crystal Mn-doped ZnS (ZnS:Mn) centered at 580 nm was investigated. The PL was quenched by surface modification with I2- treated poly(vinylferrocene). The effect of pH and temperature on the EL of ZnS:Mn in aqueous and butyronitrile solutions upon reduction of peroxydisulfate ion was also studied. EL of polycrystalline chemical vapor deposited (CVD) ZnS doped with Al, Cu-Al, and Mn was also observed with peaks at 430, 475, and 565 nm, respectively. In all cases, the EL efficiency was about 0.2%-0.3%.

Luminescence studies of semiconductors immersed in liquids provide a useful probe of surface recombination and other surface processes. For example, electroluminescence (EL) at chalcogenide semiconductor electrodes [e.g., CdS, CdSe, and CdTe (1)] has been the subject of a number of studies. Single-crystal ZnS has also been used in EL studies (2). ZnS is a wide bandgap (3.66 eV) II-VI compound semiconductor and an excellent EL material (3). Previous experimental results (1-3) suggested that it would be of interest to examine the EL of ZnS as a probe of the energetics at the ZnS/electrolyte interface and for possible application to display devices (2a).

Mn-doped (ZnS:Mn) is an efficient luminescent inorganic solid (4). Manganese is an efficient luminescence activator in a number of host lattices, e.g., silicates, sulfides, and fluorides of zinc or cadmium (5), and plays an important role in the electroluminescence of group II-VI compounds. Although much work has been done over the last * Electrochemical Society Active Member.

few decades to understand the photoluminescence (PL) and EL mechanisms in Mn luminescence centers and in group II-VI compounds doped with Mn, no work has been reported on the EL of ZnS:Mn in liquid junction cells. This paper concerns the EL at ZnS:Mn electrodes in aqueous solutions where emission typical of manganese was observed at 580 nm. A general strategy for designing optically coupled sensors with chemical specificity has attracted much attention (7), and photoluminescence from surface-modified ZnS:Mn has been studied for this purpose. We also studied EL of ZnS:Mn in a butyronitrile solution containing persulfate at different temperatures and have shown that the spectral distribution of EL is independent of temperature. The EL efficiency of ZnS:Mn in persulfate solution was found to be 0.3%. Finally, commercially available single-crystal ZnS is expensive, because it is difficult to grow high-quality, large-area, single crystals of ZnS. Large-area polycrystalline materials can be grown by chemical vapor deposition (CVD). Experi-