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CRITICAL RE-EVALUATION OF THE PHOTOEMISSION RATE LAW AT THE p-GaAs/AQUEOUS ELECTROLYTE INTERFACE

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Abstract Threshold photoemission currents at 365 nm from etched single crystal p-GaAs to 0.1M KCl electrolytes follow a 3/2 rate law in the presence of N_2O scavenger. Surface film formation decreases efficiencies with time and together with adsorbates, may cause scattering of electrons produced by direct bulk excitation. Theoretical models are discussed and compared to known photoemission behavior at semiconductor/vacuum interfaces.

INTRODUCTION

Photoemission of electrons from metallic electrodes into aqueous solutions has been widely studied and experimental techniques developed to demonstrate a 5/2 rate law, e.g.[1-6,10]. However, for the case of semiconductor electrodes very little work has been done in spite of the fact that the energy (wavelength, voltage)/current theoretical form is equivocal. Photoemission spectroscopy has been proposed for the study of surface states as well as for radical reaction studies with semiconductors [7,8,10]. In 1972, Gurevich [9,10] proposed the "3/2-rate law" for photoelectron emission from semiconductors into electrolytes, with the following theoretical expression for the photoemission current,

$$i_p = C(h\nu-E_g-\chi)^{3/2} \text{ for } h\nu > E_g + \left(\frac{m_v + m_c}{m_v}\right)\chi \qquad (1)$$

in which h is Planck's constant, ν is the frequency of excitation, E_g is the semiconductor band gap, χ is the electron affinity with respect to a solvated electron in the electrolyte, C is independent of the energy difference, m_v is the effective mass of the initial electrons in the valence band, and m_c is the effective electron mass in the conduction band. Subsquently, Pleskov and coworkers presented experimental results to support this law for the cases of p-Ge and p-GaAs in KCl and LiCl electrolytes[11,12,13]. Nevertheless, these pioneering studies made no attempt to assess experimentally contributions from surface states or from indirect transitions, and no evaluation of the conditions of the semiconductor surfaces was attempted. It should be noted that the form of the three-halves rate law from Gurevich's quantum-mechanical approach coincides with a special case for the photoemission from semiconductors into vacuum presented by Kane in 1962[14].

Gurevich also has derived a theoretical expression for photoemission from surface states which predicts that these photocurrents will obey a "3/2-law". More recently, Bockris and Uosaki[15,16,17,18] have proposed a generalized photoelectrochemical kinetic theory in which the charge transfer from a semiconductor to an acceptor in the electrolyte is the rate-determining step and the predicted rate law for classical photoemission is given by

$$i_p = e_o \frac{C_A}{C_T} \{ \int_{U_m}^{\infty} N_e(E)dE \} \qquad (2)$$

in which C_A and C_T are the total number of acceptors and sites respectively per unit area of the outer Helmholtz plane, $N_e(E)$ is the number function for photoexcited electrons decreased by electron-electron or electron-phonon scattering and modified by the density of states distribution and optical attenuation, and U_m is the maximum value of the barrier height (corrected for solvation energy, image forces, and optical Born charging). The contribution of photocurrents due to electron tunneling through the barrier may cause an additional contribution to the photocurrents. There have been some other recent investigations of photoelectron injection into electrolytes, but these examine the fate and energetics of the solvated electrons rather than the process rate laws[19,20,21].

The objective of this study is to examine critically the experimental rate law for photoemission from p-GaAs into aqueous electrolyte using near-ultraviolet radiation. If the bulk (volume) excitation follows the same rate law as that of surfaces states, then the separation of these two processes will become more complex.

EXPERIMENTAL

To obtain ohmic contact, the Zn-doped (100) p-GaAs single crystals (N_D=1.7x10^{18}cm^{-3}) were electroplated with Cu on an exposed face. Masking of the non-exposed faces was achieved with a soluble varnish. Wires were attached using a Ag-based conductive cement (Johnson Mathey). Insulation was provided with a thin varnish film coated with paraffin wax. Before each experiment, the electrodes were etched chemically by immersion for 5 min. in 5 wt % NaOH: 30 vol % H_2O_2 in volume ratio 5:1, followed by 30 secs in c.HF:c.HNO_3:H_2O in volume ratio 1:3:2, thorough rinsing in water, and finally a rinse in the electrolyte 0.1M KCl. Electrolytes were prepared from doubly recrystallized salt and distilled water from a continuous Gilmont still (MOD V). A combination pH/SCE electrode was used for reference with a small Pt wire counter electrode distanced from the working electrode. The quartz cell, fitted with standard taper joints for electrodes and gas ports, was leached in 20% $HCl/HNO_3/H_2O$ solution for at least 24 hours to diminish trace impurities. Argon was used to deoxygenate the electrolyte and was purified with vanadous ion scrubbers. The elimination of traces of oxygen and adventitious impurities is important, as they react with the photoemitted electrons. Experiments were made at pH 7.4 and 11.4 to minimize hydrogen ion photocurrents.

Optical radiation was obtained using a 250W Hg lamp (Ealing Corp.). The wavelength was selected in some cases with a blue filter (Corning 5543-7-51), which is transparent between 300-400 nm with %T max at about 360 nm. Alternatively, a Jarrell-Ash monochromator model Mark X set at 365 nm was used to provide lower light intensities. Quoted intensities are estimated from measurements with a UDT 111A Photometer/Radiometer (uncalibrated).

Typical experiments were performed as follows. Immediately after etching, a crystal was immersed into an electrolyte thoroughly degassed with Ar. After 5 min, the gas bubbling was stopped and several cyclic scans were made until reproducible waveforms were obtained (this removes reducible oxide film or adsorbed oxygen). Degassing was continued and subsequent scans repeated at intervals. In some experiments, N_2O was bubbled to flush the system of Ar and scan experiments were made on the aged p-GaAs substrate. In others, the crystals were re-etched and parallel sets of measurements were taken in time.

A schematic of the apparatus to record photoemission currents is shown in Figure 1. Linear sweeps from a PAR Model 175 Universal programmer were imposed to the three-electrode cell with a PAR model 173/179 potentiostat/ digital coulometer. Photocurrents were digitalized with a Tektronix 468 oscilloscope and/or recorded by X-Y recorder (PAR model 9002A). The oscilloscope was interfaced via its IEEE 488 bus to an IBM Instruments CS/9000 microcomputer. Software for data input made use of the extended I/O facilities for BASIC. Least square iterative calculations also were programmed in BASIC. The best fits to the linearized form of the photocurrents were determined from the calculated correlation coefficients.

RESULTS

Figure 2 illustrates a typical experiment, in which the lower curve represents the onset of photocurrents obtained in the presence of Ar. These currents comprise reactions

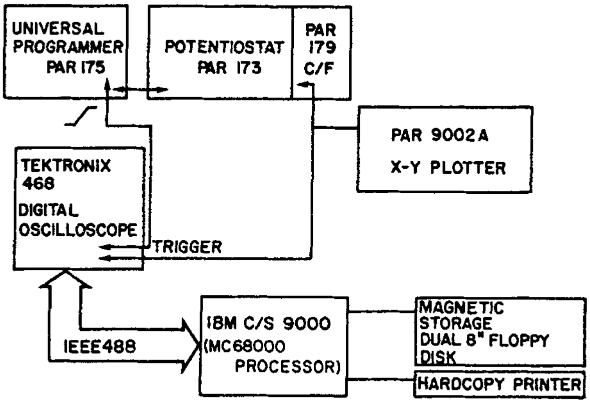

FIGURE 1. Electrochemical and Data Acquisition Equipment

at the band edge (photofaradaic) and reactions of impurities (and proton) with solvated electrons. The first scan under illumination causes a photoassisted irreversible reaction of surface compound. The upper curve includes the former contributions, together with photocurrents obtained by the irreversible reactions of solvated electrons with dissolved N_2O. It is assumed that the photoemission rates are proportional to this current density difference, as follow-up electron transfer reactions will be directly proportional to the irreversible scavenger reaction rate[10].

$$e^-_{solv} + N_2O + H_2O \rightarrow N_2 + OH^- + OH^\bullet \qquad (3)$$

$$OH^\bullet + e^-_{surf} \rightarrow OH^- \qquad (4)$$

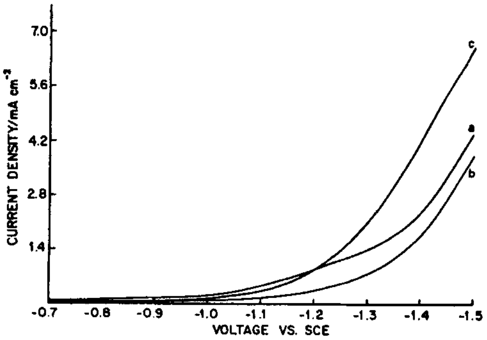

FIGURE 2. Ar first scan (a), Ar second scan (b), N_2O scan (c) at 20 mVs^{-1}, area 0.71 cm^2, 365 nm intensity 18x10^2 μW cm^{-2}, pH 7.4.

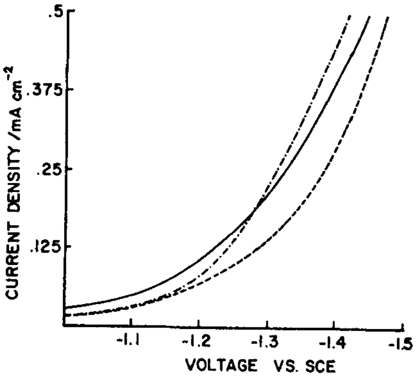

FIGURE 3. N_2O/Ar difference currents at scan rates 20(-.-.), 50(——), and 200(----)mVs^{-1}, pH 11.4 (other conditions as figure 2).

It is assumed that currents arising in chemical pathways (N_2O catalytic currents) can be ignored under illumination conditions[8]. Figure 3 contains the net photocurrents in 0.1 M KCl electrolyte as a function of scan rate. The small current differences with scan rate may be due largely to charging (capacitive) current effects.

The results of attempts to fit the current differences raised to different exponents, $(i_{N_2O}-i_{Ar})^p$ are illustrated in Figure 4, and much lower values of the regression coefficient resulted from attempts to fit a logarithmic function. These calculations were made to include foot-of-the-wave currents, typically for the voltage range -1.100 V to -1.500 V vs SCE. Figure 5 exemplifies the dependence of the regression coefficient (r) with exponent (p). Although there may be physical reasons to ignore the foot of wave(**vide infra**) this represents fit of data over a wider range than that reported by earlier workers [10,11,12,13]. The result of experiments obtained on the aged substrates,(5 min. Ar flush and 25 min. N_2O flush) are as follows, pH 7 4:p = 0.66 ± 0.17 (15 experiments), pH 11.4:p = 0.60 ± 0.09 (15 experiments). The least square intercept was calculated to be 1.08 ± 0.07 V(SCE). Experiments on etched surfaces for equivalent short periods of immersion in either Ar or N_2O saturated electrolytes are consistent with these results. However, in cases where the crystal was left for extended periods of time in the solution (>1hr), the photoemission currents and best exponents are smaller and a white film can be visually observed to coat the surface (Figure 6).

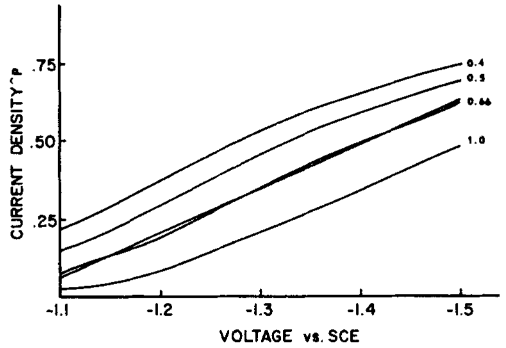

FIGURE 4. Least squares fit of exponents, p.

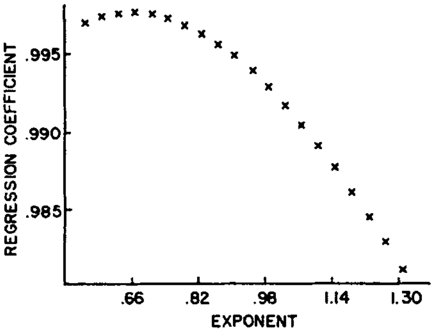

FIGURE 5. Regression coefficient vs. exponent, n.

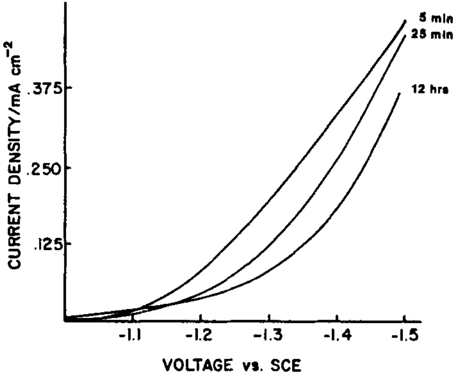

FIGURE 6. Time dependence of difference currents, pH 11.4 (other conditions as Figure 2).

DISCUSSION

Photoemission of electrons may be considered as a three step process - the absorption of an incident photon that has penetrated the bulk of the semiconductor, the escape of the excited electron into the electrolyte, and the subsequent capture of the solvated electron.

There is no reason to believe, apart from threshold energy modifications, that the internal processes are different from those for the semiconductor/vacuum system. Although the absorption depth of light may be about 120 Å in GaAs, the actual escape depth of electrons may be small, about 25 Å if analogous to the vacuum cases[22]. This is of the order of magnitude of the depletion layer, about 30 Å in this example, assuming an approximately 1 volt potential drop across the layer at threshold. Gobelli and Allen[23] have demonstrated experimentally that the threshold function must be modified for p-type materials whose bands are bent upwards with increasing penetration. This effect has not been accounted for in the theory of Gurevich, although our results obtained for photoemission from p-GaAs into 0.1M KCl at pH 7.4 and 11.4 agree with those reported earlier, and are consistent with an overall "3/2 rate law," cf. [12,13]. However, caution should be exercised in using these result to support a theoretical 3/2 law for direct excitation of electrons from bulk crystal. It is well known that narrow band gap III-V semiconductors form pH dependent surface compounds and films,[24]. Vacuum studies of semiconductors have demonstrated that nitrogen or oxygen interactions on the "clean" surfaces of cleaved crystals can produce drastic changes in the rate law and efficiencies of photoemission. At p-GaAs/aqueous 0.1M KCl, measurements of photocurrents provide evidence of time dependent surface effects, (Figure 6). Undoubtedly, interfacial compound formation and filming are present at the semiconductor/aqueous electrolyte junctions investigated thus far. The general problems, therefore, are to distinguish bulk photoemission currents from those arising in surface layers or films, and to establish the influence of the surface on the initial bulk contribution to the net photocurrents. In other words, it is important to determine the extent of electron scattering by interfacial compounds and that of the solution. Experiments in other electrolytes [non-aqueous] may be helpful in this regard and necessary before progress in quantifying these surface and double layer effects is possible.

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