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PHOTOELECTROCHEMICAL EVIDENCE FOR SATURATED OPTICAL
ABSORPTION IN ELECTROLYTIC CUPROUS OXIDE

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PHOTOELECTROCHEMICAL EVIDENCE FOR SATURATED OPTICAL ABSORPTION IN ELECTROLYTIC CUPROUS OXIDE

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Abstract

An illuminated cuprous oxide-covered electrode immersed in alkaline media exhibits a nonlinear dependence of photocurrent on the intensity of 488 nm laser illumination. Results from intensity modulation experiments show that the differential efficiency for converting photons to photocurrent in the p-type cuprous oxide thin film is inversely proportional to the square root of illumination intensity. A charge transfer model that includes intensity-dependent optical absorption in the cuprous oxide layer is found to be consistent with the observed photocurrent response. Analysis of the experimental results using the charge transfer model shows that the saturation intensity for cuprous oxide is approximately 100 mW/cm^2 . Photoelectrochemical charge transfer is found to be efficient in the potential region where the nonlinear photocurrent response is observed, with nearly all photo-injected minority carriers being consumed by the interfacial charge transfer reaction rather than by recombination.

Photoelectrochemical (PE) techniques measure changes in the current (photocurrent) or potential (photopotential) when an electrode is illuminated. These techniques are often used in conjunction with models to derive solid-state properties (e.g. band gaps,¹ optical absorption coefficients,² surface state energies,³ etc.) for semiconductor/electrolyte interfaces and to identify the composition of semiconducting surface films. Metal-oxides often form PE junctions when contacted with electrolyte;⁴ cuprous oxide (Cu_2O) is one such material.⁵ The monovalent surface film on copper electrochemically oxidized in alkaline media is a thin (≤ 10 nm),^{6,7} semiconducting cuprous oxide layer with p-type conductivity.⁶⁻⁸ Recently, we showed in a laser Raman spectroscopy and PE study of film formation on copper electrodes that the cathodic photocurrent from a cuprous oxide-covered surface exhibits a nonlinear dependence on illumination intensity when subject to a 488 nm laser probe beam.⁸ In this Letter, the intensity-dependent photocurrent from an electrolytic cuprous oxide thin film is found to agree with a charge transfer model where optical absorption is saturated by the laser beam.

Cuprous oxide thin films are prepared by oxidizing a small area ($\sim 5 \times 10^{-4} \text{ cm}^2$), high purity (99.999%) copper electrode in 1M KOH electrolyte at room temperature. The potential (E) of the copper electrode relative to a Hg/HgO reference is slowly increased (1 mV/s) up to the oxygen evolution potential (near 600 mV), where the surface is covered by a divalent film. The potential scan direction is then reversed and the surface film is reduced. Shown in Fig. 1 is the current as a function of potential when the copper electrode is illuminated by a mechanically chopped (5 seconds on, 55 seconds off) 488 nm laser beam (intensity $\approx 250 \text{ W/cm}^2$). Positive current denotes oxidation reactions and negative current denotes reduction reactions. Figure 1 shows that the surface films on copper are photoelectrochemically active during certain portions of the potential scan. The largest photocurrent "spikes" are observed from -0.3 V to -0.7 V as the potential scans to more negative values; this is the potential region where the photocurrent dependence on illumination intensity is nonlinear.⁸ In this potential region, charge transfer is mediated by a thin cuprous oxide film covering the copper substrate.⁷⁻⁹ The large cathodic photocurrent spikes observed in Fig. 1 confirm that the cuprous oxide film is a p-type semiconductor.

In order to measure the effect of illumination intensity on photocurrent, intensity modulation experiments have been performed. The oxidation films used in the intensity modulation experiments are prepared as described above. The electrode is illuminated with an intensity-modulated 488 nm laser probe beam, $I(t) = \bar{I}[1 + \epsilon \cos(\sigma t)]$, where $I(t)$ is the intensity incident on the sample, $\bar{I}$ is the mean intensity, $\epsilon \approx 0.1$ is the modulation amplitude, and $\sigma = 50$ Hz is the modulation frequency. The intensity modulation induces an a.c. photocurrent signal when the interface is photoelectrochemically active. The amplitude of the a.c. photocurrent density ($|j_{ac}|$) is

$$|j_{ac}| = \epsilon \bar{I} \frac{\partial j_{ph}}{\partial I}(\bar{I}, U) \quad (1)$$

when $\epsilon \ll 1$ and $1/\sigma \gg \tau$, where τ is the characteristic relaxation time for the interface, j_{ph} is the d.c. photocurrent density, and U is the potential drop across the space charge layer. The amplitude of the a.c. photocurrent is measured with a lock-in amplifier synchronized to the modulated laser intensity and the photocurrent *density* is calculated by dividing the measured photocurrent with the area illuminated ($8 \times 10^{-5} \text{ cm}^2$, estimated on the basis of beam profile measurements).

Plotted in Fig. 2 is the a.c. photocurrent density signal, $|j_{ac}|$, over the potential range -0.25 V to -0.8 V for different values of the mean illumination intensity, $\bar{I}$. The reported illumination intensities are based on measurements of the beam power, and estimates for illuminated area and reflection losses at the electrochemical cell window. A maximum in the a.c. photocurrent density is found near -0.5 V for each curve in Fig. 2; the location of the maximum is consistent with the results in Fig. 1. Figure 2 shows that attenuating the intensity of the 488 nm probe beam from $\sim 250 \text{ W/cm}^2$ in curve (a) to $\sim 0.31 \text{ W/cm}^2$ in curve (d) only reduces the a.c. photocurrent peak height by an order of magnitude. This result shows that the differential efficiency for converting photons to photocurrent ($\partial j_{ph}/\partial I$) increases as the illumination intensity decreases. The intensity-dependent a.c. photocurrent density observed in Fig. 2 is not characteristic of a charge carrier-limited PE reaction, where the a.c. signal is expected to be linear with $\bar{I}$, nor is the a.c. signal negligible as expected for a redox species-limited reaction.

A model for charge transfer must be developed for the potential region near -0.5 V in order to compare Eq. (1) with the measured a.c. photocurrent density. Since the thickness of the

cuprous oxide layer ($L \leq 10$ nm)⁶⁻⁹ is smaller than any other pertinent length-scale for the interface (i.e., optical absorption, space charge layer, charge carrier diffusion), it has been proposed that the d.c. photocurrent density for a reverse biased cuprous oxide/alkaline media junction is given by⁹

$$j_{ph} = (1+R)q_0L\alpha\eta I/\hbar\omega, \quad (2)$$

where R is the reflection coefficient for the copper/cuprous oxide interface, $q_0 = 1.6 \times 10^{-19}$ (C) is the electron charge, α (cm^{-1}) is the optical absorption coefficient of cuprous oxide, $\eta = \eta(U)$ is the bias-dependent charge transfer efficiency (fraction of photo-injected minority carriers that escape recombination and are consumed by charge transfer), and $\hbar\omega$ (J) is the photon energy. Equation (2) is a charge carrier-limited model for the interface, therefore substituting (2) into (1) provides an equation for the a.c. photocurrent density that is linear with $\bar{I}$. This is not the intensity dependence observed in Fig. 2. In substituting Eq. (2) into (1), α was assumed to be independent of illumination intensity; this assumption may not be valid for the energy and intensities of the laser beam employed here.

The 488 nm illumination used in this study is close in energy to that needed for an interband transition in cuprous oxide, leading to exciton absorption¹⁰ and resonance enhanced Raman scattering^{11,12} in the material. Optical absorption of photons with resonant energies often depends on the illumination intensity. A common form for the intensity-dependent absorption coefficient is $\alpha(I) = \alpha_0/[1+I/I_s]^n$, where $\alpha_0 = \alpha_0(\omega)$ is the low intensity optical absorption coefficient, $I_s = I_s(\omega)$ is the saturation intensity, and n (equal to 1/2 or 1) is a constant that depends on the saturation model employed.^{13,14} A value of $n=1/2$ is used for the saturation of direct transitions between broadened energy levels.¹³ Inserting $\alpha(I)$ into Eq. (2) and differentiating with respect to intensity provides an expression for the differential photon-to-photocurrent efficiency,

$$\frac{\partial j_{ph}}{\partial I}(\bar{I}, U) = \{2q_0L\alpha_0\eta(U)/\hbar\omega\} \left([1+\bar{I}/I_s]^{-1/2} - 0.5(\bar{I}/I_s)[1+\bar{I}/I_s]^{-3/2} \right), \quad (3)$$

where $n=1/2$, $R=1$, and $\partial\eta/\partial I=0$ have been assumed. Equation (3) shows that $\partial j_{ph}/\partial I$ is independent of illumination intensity for $\bar{I}/I_s \ll 1$ and is inversely proportional to the square root of intensity for $\bar{I}/I_s \gg 1$.

Plotted in Fig. 3 is a quantitative comparison of experimental and theoretical values for $\partial j_{ph}/\partial I$ as a function of laser intensity. The filled circles denote experimental values for $\partial j_{ph}/\partial I$ obtained by dividing the $|j_{ac}|$ peak height for each curve in Fig. 2 by $\epsilon \bar{I}$, see Eq. (1). The error bars on the data points are estimates based on the range of peak heights found for repeat runs at the highest intensity. The solid line in Fig. 3 is the high intensity limit ($\bar{I}/I_s \gg 1$) of Eq. (3):

$$\frac{\partial j_{ph}}{\partial I}(\bar{I}, U) = \{q_0 L \alpha_0 \eta / \hbar \omega\} [\bar{I}/I_s]^{-1/2}. \quad (4)$$

The agreement between Eq. (4) and the experimental points (●) suggests that saturated optical absorption is responsible for the nonlinear intensity dependence of the a.c. photocurrent. The slope of the theoretical line in Fig. 3 is -1/2 (this is dictated by the value of n); the only adjustable parameter is a single lumped constant. The best-fit of Eq. (4) to the experimental points in Fig. 3 is found when $\{q_0 L \alpha_0 \eta / \hbar \omega\} I_s^{1/2} \approx 100 \mu A / (W^{1/2} cm)$. Using physically reasonable values for L and α_0 ($10^{-6} cm$ and $10^3 cm^{-1}$, respectively)^{6,9} in the best-fit constant gives $\eta I_s^{1/2} \approx 0.3 W^{1/2} / cm$. It is evident from Fig. 3 that all of the experimental points were acquired in the high intensity regime ($\bar{I}/I_s \gg 1$), therefore $I_s < 1 W/cm^2$. Moreover, the charge transfer efficiency must satisfy the constraint $\eta \leq 1$. An order of magnitude estimate for η and I_s that satisfies all experimental and physical requirements of this system is $\eta \approx 1$ and $I_s \approx 0.1 W/cm^2$. No other set of physically reasonable values for η and I_s will meet all of the above criteria. Past photocurrent studies of bulk cuprous oxide showed that $\partial j_{ph}/\partial I$ was constant for low illumination intensities ($\lambda = 470 nm$),⁵ as predicted by Eq. (3), and a charge transfer efficiency of $\eta \approx 1$ has been used by others to determine the energy-dispersion of optical absorption in cuprous oxide.⁹ The room temperature saturation intensity found in this work, $I_s \approx 0.1 W/cm^2$, is low even compared to typical values for quantum well structures;¹⁴ direct measurements of optical absorption in cuprous oxide thin films are warranted to verify this saturation intensity. Nevertheless, the agreement between the experimental results and the intensity-dependent optical absorption model for charge transfer provides the first evidence for low-intensity saturated optical absorption in cuprous oxide thin films.

In conclusion, it was shown that the photoelectrochemical activity near -0.5 V (vs. Hg/HgO) depended nonlinearly on the illumination intensity of a 488 nm laser beam. The

photocurrent nonlinearity was interpreted using a charge transfer model that included intensity-dependent optical absorption in the cuprous oxide surface layer. The a.c. photocurrent density amplitude from a reverse biased cuprous oxide-covered surface was found to be proportional to the square root of intensity when illuminated with a 488 nm laser probe beam having intensities greater than 100 mW/cm². Fitting the experimental data to theory showed that the charge transfer efficiency for the cuprous oxide/alkaline media junction was near unity.

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REFERENCES

- ¹M.A. Butler, J. Appl. Phys. **48**, 1914 (1977).
- ²L.M. Peters, Ber. Bunsenges. Phys. Chem. **91**, 419 (1987).
- ³R.H. Wilson, J. Appl. Phys. **48**, 4292 (1977).
- ⁴S.R. Morrison, "*Electrochemistry at Semiconductor and Oxidized Metal Electrodes*" (Plenum Press, NY, 1980).
- ⁵H.R. Schoppel and H. Gerischer, Ber. Bunsenges. Phys. Chem. **75**, 1237 (1971).
- ⁶M. Yamashita, K. Omura, and D. Hirayama, Surf. Sci. **96**, 443 (1980).
- ⁷U. Collisi and H.-H. Strehblow, J. Electroanal. Chem. **210** (1986) 213.
- ⁸D.T. Schwartz and R.H. Muller, Surf. Sci., submitted.
- ⁹L.M. Abrantes, L.M. Castillo, C. Norman, and L.M. Peters, J. Electroanal. Chem. **163**, 209 (1984).
- ¹⁰A. Golzene and C. Schwab, in *Landolt-Bornstein, Physics of Non-Tetrahedrally Bonded Elements and Binary Compounds I*, Edited by O. Madelung, (Springer-Verlag, Berlin, 1983), Vol. 17e, p. 144.
- ¹¹Y. Petroff, J. de Phys. Colloque C-3 **35**, 277 (1974).
- ¹²J.C. Hamilton, J.C. Farmer, and R.J. Anderson, J. Electrochem. Soc. **133**, 739 (1986).
- ¹³A.A. Borshch, M. Brodin, V. Volkov, "*Refractive Nonlinearity of Wide-Band Semiconductors and Applications*", Edited by V.S. Letokhov, C.V. Shank, Y.R. Shen, and H. Walther, (Harwood Academic Press, Chur, Switzerland, 1990), §1.5.
- ¹⁴D.S. Chemla, D.A.B. Miller, P.W. Smith, A.C. Gossard, and W. Wiegmann, IEEE J. Quantum Electron. QE-20, 265 (1984).

FIGURE CAPTIONS

FIG. 1. Current versus potential for a copper electrode in 1 M KOH electrolyte. Current spikes result from illumination with 5 second pulses of a 488 nm laser beam ($\sim 250 \text{ W/cm}^2$).

FIG. 2. Dependence of the a.c. photocurrent density on potential near -0.5 V for different illumination intensities. The mean illumination intensities are $\bar{I} \text{ (W/cm}^2\text{)} \approx$ (a) 250, (b) 31, (c) 2.5, and (d) 0.31. The three pairs of horizontal lines denote shifted zeros for curves (b)-(d). The ordinate scales for curves (a)-(d) are different; peak heights ($\mu\text{A/cm}^2$) are given for each curve.

FIG. 3. Decrease of photon-to-photocurrent conversion efficiency with increasing laser illumination intensity. Experimental points are obtained from the peak heights in Fig. 2, see Eq. (1), and the solid line is calculated using Eq. (4) with $L=10^{-6} \text{ cm}$, $\alpha_0=10^3 \text{ cm}^{-1}$, $\eta=1$, and $I_s=0.1 \text{ W/cm}^2$.

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FIG. 1. Current versus potential for a copper electrode in 1M KOH electrolyte. Current spikes result from illumination with 5 second pulses of a 488 nm laser beam ($\sim 250 \text{ W/cm}^2$).

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FIG. 2. Dependence of the a.c. photocurrent density on potential near -0.5V for different illumination intensities. The mean illumination intensities are $\bar{I}$ (W/cm^2) = (a) 250, (b) 31, (c) 2.5, and (d) 0.31. The three pairs of horizontal lines denote shifted zeros for curves (b)-(d). The ordinate scales for curves (a)-(d) are different; peak heights ($\mu\text{A}/\text{cm}^2$) are given for each curve.

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FIG. 3. Decrease of photon-to-photocurrent conversion efficiency with increasing laser illumination intensity. Experimental points are obtained from the peak heights in Fig. 2, see Eq. (1), and the solid line is calculated using Eq. (4) with $L=10^{-6}$ cm, $\alpha_0=10^3$ cm⁻¹, $\eta=1$, and $I_s=0.1$ W/cm².

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