CHEMISTRY LETTERS, pp. 875-880, 1976. Published by the Chemical Society of Japan

ORGANO-MODIFIED METAL OXIDE ELECTRODE. I. STUDIES OF MODIFIED LAYER BY CAPACITANCE MEASUREMENTS AND ESCA

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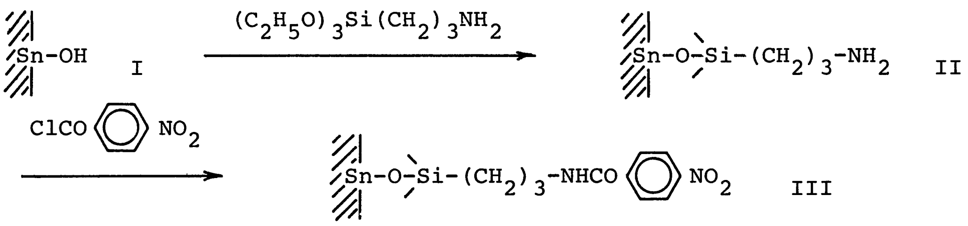
The successive chemical modifications of silanized tin oxide electrodes to the more complicated compounds have been investigated. ESCA and electrochemical techniques were employed for characterization of the organo-modified surfaces. Understanding of the semiconductor electrode-solution interfaces has been greatly advanced by the capacitance measurements of the modified electrodes.

Recently there has been a great deal of interest in the chemical modification of surfaces as means of producing selective and catalytic electrodes. Miller et al. were the first to demonstrate that a chiral electrode can be used to perform an asymmetric reduction.1) Through the methods analogous to those described by Harper for glass-bound pH indicators,2) Murray and coworkers3) demonstrated that the surface of tin oxide electrodes can be modified, as silica surfaces, by the bonding of various chemical functional groups (amine, pyridine, and ethylenediamine) via silyl ethers. The surface reactions and confirmatory chemical tests involving amine protonation and metal coordination were followed by X-ray photoelectron spectroscopy (ESCA). They also examined the electrochemical properties of these modified electrodes by cyclic voltammetry and observed lower charging currents and lower charge transfer rates on the derivatized tin oxide surfaces than on the untreated ones. This implies that the electrical double layer is greatly affected by the modification of the surfaces with low conductive organic compounds in such a way that the double layer is affected by the adsorption of surface active substances. Thus, it is worth while to study the effect of the organo-modification on the double layer capacitance. As yet no detail of capacitance measurements of the modified electrodes has been described. Preliminary results of capacitance measurements and surface analysis by ESCA and Auger of the modified tin oxide electrodes have been reported previously.4)

In this paper, the further modification of the silanized tin oxide electrode with γ-aminopropyltriethoxysilane (APTSI) to the more complicated compounds terminated with nitro functional group will be described. This has been the first step to our final objective which is to bind dyes covalently to various metal oxide semiconductors. As means of the quantitative analysis of the electroacitve functional groups, such as nitro group, bound on the surfaces, the electrochemical methods based upon Faraday's law will be presented. Results of capacitance measurements of the clean and modified electrodes will be compared and discussed in terms of the change in the Helmholtz capacitance by the modifications. Also, it will be demonstrated experimentally that the flatband potential of heavily doped SnO_2 electrodes is in agreement with those reported for SnO_2 of comparatively low carrier densities after the correction for Helmholtz capacitance proposed by De Gryse and coworkers.5) The more obvious contribution of the Helmholtz capacitance on the modified electrodes will be presented.



EXPERIMENTAL

The antimony doped tin oxide electrode was obtained from Corning Glass Co. The thickness of SnO_2 films on glass (2.6 mm thick) was ca. 800 nm as determined from interference patterns and the film resistivity was ca. 10 ohms $square^{-1}$. The alkylamine SnO_2 electrodes were prepared by the method developed by Murray and coworkers.3) G.R.-grade APTSI is commercially available from Nakarai Chemical Co. and was used without further purification. The synthetic procedure from alkylamine to nitrobenzene derivative was modified from that developed by Harper.2)

The cell design used for the electrochemical studies was similar to that previously described,6) in which a peripheral copper ring for electrical contact and an o-ring seal were used. The cyclic voltammetric experiment was carried out with a conventional electrochemical instrument. Capacitance measurements were made by the method of Gileadi and coworkers;7) a small amplitude (50 mV) triangular wave of 500 Hz or 1 kHz was superimposed on a constant applied potential. For ESCA analysis, an AEI Model ES 200 was used. Binding energies were computed and corrected for charging effect by referencing to the 285 eV C 1s peak,8,9) though it is significant only as a relative reference.10)

Solution was prepared by using doubly distilled water and G.R.-grade chemicals.

RESULTS AND DISCUSSION

An ESCA spectrum of the clean SnO_2 (I) is shown in Fig. 1, together with a spectrum of the propylamine derivative (II). The spectrum of I contains strong peaks for O 1s at 530.5 eV, Sn $3d_{3/2}$ at 495 eV, Sn $3d_{5/2}$ at 486 eV, Sn 4d at 25 eV, and C 1s at 285 eV. The C 1s peak of ca. 1300 counts s^{-1} results from the contamination carbon and appears on all samples. In addition to these peaks due to oxygen, tin, and carbon, new peaks for N 1s at 400 eV, Si 2s at 154 eV, and Si 2p at 103 eV appear on the spectrum of II as expected from its chemical formula. Being treated for longer time or treated in a solution of higher APTSI concentration, the propylamine SnO_2 electrodes exhibited higher N 1s, Si 2s, and Si 2p peaks and lower Sn 3d and Sn 4d peaks than those on the spectrum of II in Fig. 1, as a consequence of the increase in surface coverage of the overlaying molecules.$^{3)}$ An ESCA spectrum of the nitrobenzene derivative (III) is similar to that of II and also shows N 1s, Si 2s, and Si 2p peaks, but the N 1s appears as a doublet. The binding energies for Sn 3d, C 1s, Si 2s, Si 2p, and Sn 4d electrons were unchanged throughout the series of modified surfaces, but the shape of O 1s band of the clean SnO_2 (peak at 530.5 eV with a shoulder at 532 eV) was changed by the silanization. On the modified electrodes, O 1s peak at 532 eV is predominant and the peak at 530.5 eV of the clean SnO_2 appears as a shoulder of the main peak. The peak at 530.5 eV was assigned to

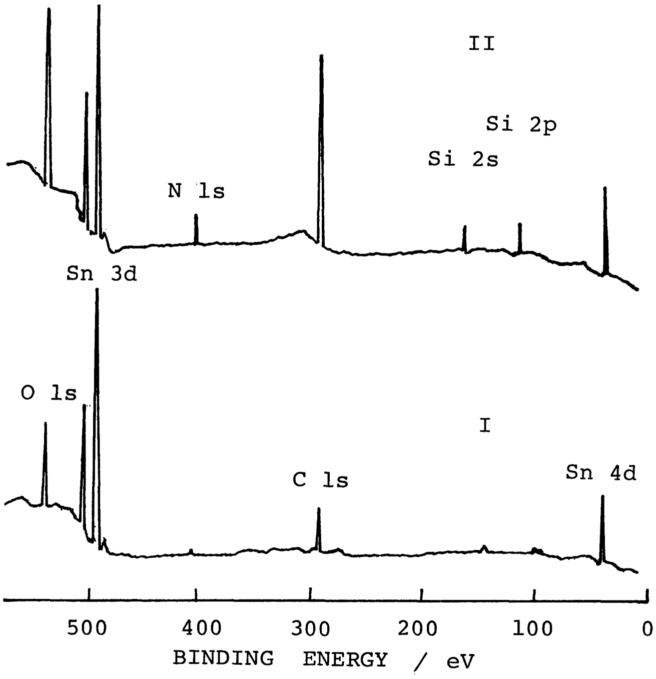


Fig. 1. ESCA spectra of clean SnO_2 (I) and propylamine derivative (II).

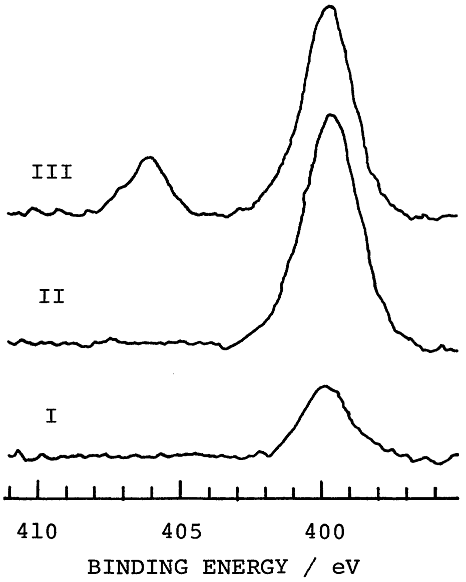


Fig. 2. ESCA N 1s spectra for clean SnO_2 (I), propylamine derivative (II), and nitrobenzene derivative (III).

the oxide O 1s of SnO_2[4,11)] and the peak at 532 eV may be assigned to -OH and -O-Si-R on the surfaces. Details of the discussion will be reported elsewhere.

In order to show whether the modifications of the surfaces are successful or not, the change in ESCA N 1s spectra of the successively modified electrodes is shown in Fig. 2. From bottom to top, N 1s peaks for the clean SnO_2 (I), the propylamine (II), and the nitrobenzene derivatives (III) are shown. Even on the clean SnO_2 at 5×10^{-9} Torr, a small N 1s peak was observed. From its binding energy, the nitrogen contaminations on the surface, which may be introduced during the process of pretreatment, can be considered to be present as reduced forms such as amine. After the silanization reaction with APTSI, N 1s peak at 400 eV increased as a result of the addition of the amine structure on the SnO_2 surface. If the amine underwent condensation with p-nitrobenzoyl chloride in a 100 % yield, a doublet of equal peak heights (N 1s of nitro group at 406 eV and N 1s of amide group at 400 eV) should result from analogy with an ESCA spectrum of p-nitrobenzamide.[12)] The ESCA N 1s spectrum of III in Fig. 2 indicates that part of the amine remained unreacted even on the sample treated for a week, though higher yield of the nitro group introduction was obtained in comparison with the results of the surfaces treated for 24 hrs.[13)]

The cyclic voltammograms at the derivatized electrodes show lower charging currents than that at the clean tin oxide electrode as shown in Fig. 3. For the nitrobenzene derivative (III), a cathodic peak appeared at -0.65 V vs. SCE in the first sweep and disappeared in the subsequent sweeps. This peak may be assigned to the irreversible reduction of the surface-bound nitrobenzene derivative. Surface coverage less than 20 % for the nitrobenzene derivative was calculated from the area surrounded by the first and second sweeps, which agreed with the ESCA results. The result indicates that the electroactive functional groups bound on the surfaces can be more easily detected by the cyclic voltammetry than by ESCA.[14)] The application of the modified electrodes to trace analysis will be reported elsewhere.

The measured differential capacitance C of the semiconductor electrode-solution interface can be written generally as[15)]

$$C^{-1} = C_s^{-1} + C_H^{-1} + C_G^{-1} \qquad (1)$$

where C_s, C_H, and C_G are the space charge capacitance, the Helmholtz capacitance, and the Gouy capacitance. The last C_G^{-1} term in Eq. (1) can be neglected in the present case where 1 M Na_2SO_4 was used. On the other hand, the carrier concentration of the n-type SnO_2 semiconductor used is the order of 10^{20} cm^{-3}, thus the contribution of the Helmholtz capacitance C_H to the measured capacitance C should be taken into account as De Gryse

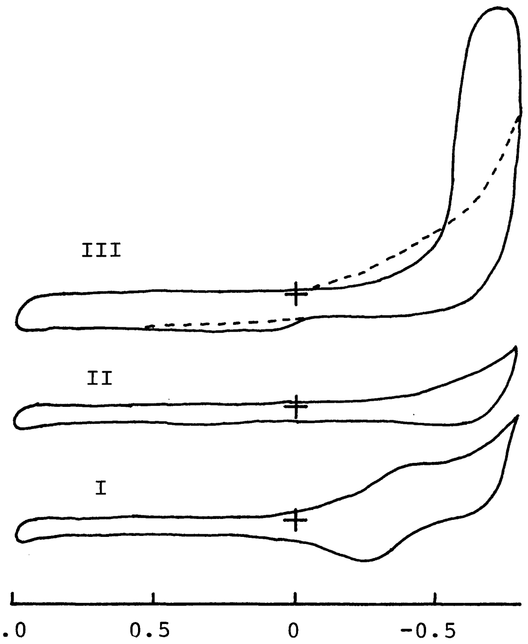


Fig. 3. Cyclic voltammograms of I, II, and III, scan rate: 360 mV s^{-1}.

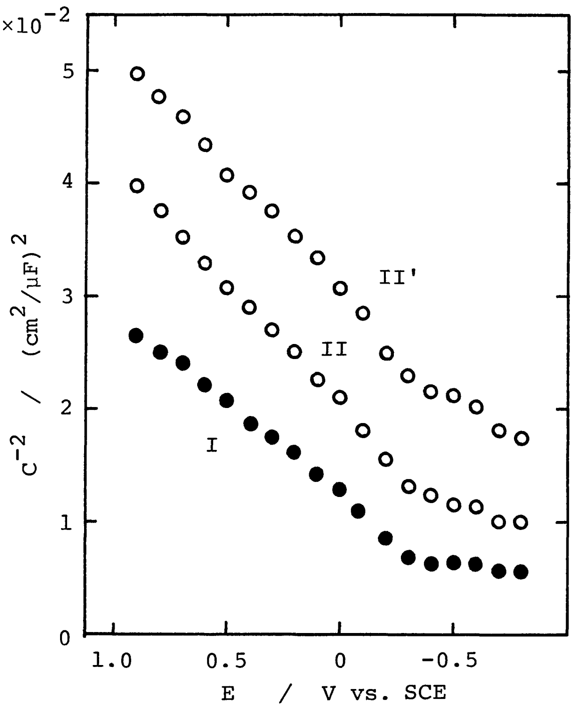


Fig. 4. C^{-2} vs. E plots for clean (I) and propylamine derivatives (II and II').

and coworkers pointed out.[5)] In such a system, C^{-2} can be written, instead of the Mott-Schottky relationship, as,[5)]

$$C^{-2} = (2/q\varepsilon\varepsilon_0 n_0)(E - E_{fb} - kT/q) + C_H^{-2} \qquad (E > E_{fb}) \qquad (2)$$

where q is the electronic charge, ε is the dielectric constant for SnO_2, ε_0 is the permittivity in vacuum, n_0 is the carrier concentration. In the more cathodic potential region than the flatband potential E_{fb}, the Helmholtz capacitance becomes predominant and C may be independent of the potential.

Consequently, usual C^{-2} vs. E plot is shifted upward in parallel by C_H^{-2} and the intersection of the simple extrapolation with potential axis cannot be used for the calculation of the flatband potential. Instead, the potential where C^{-2} vs. E plot inflects should be used for the calculation of E_{fb}, while the carrier concentration can be calculated from the slope. As shown in Fig. 4, C^{-2} vs. E plot of the clean SnO_2 (I) behaves as predicted and E_{fb} ca. -0.4 V vs. SCE is calculated from the inflection point, which is in agreement with those reported for SnO_2 of low carrier densities (10^{18}-10^{19} cm^{-3}) by Memming and Mollers.[16)] Thus, the discrepancy of E_{fb} reported for SnO_2 of high carrier densities (10^{20}-10^{21} cm^{-3})[16,17)] can be attributed to an error in the determination of E_{fb} by simple extrapolation of C^{-2} vs. E plots.

If the electrode surface is modified with low conductive organic compounds, the Helmholtz capacitance decreases because of the increase in the Helmholtz layer thickness. As shown in Fig. 4, C^{-2} vs. E plot moves upward in parallel with the increase in degrees of silanization of the propylamine derivative (II). From the inflection points of C^{-2} vs. E plots for the propylamine derivatives, E_{fb} ca. -0.4 V vs. SCE was obtained, which is almost the same as that of the clean SnO_2. Although the slope for the well treated propylamine derivative is slightly steep compared with the slope for the clean SnO_2 as reported previously,$^{4)}$ it may be attributed to the potential dependence of the Helmholtz capacitance, as is observed in the cathodic potential region in Fig. 4, rather than to the change in the carrier density.

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(Received June 9, 1976)