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Analysis of nonlinear Mott-Schottky plots obtained from anodically passivating amorphous and polycrystalline TiO_2 films

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The present work is concerned with analysis of the nonlinear Mott-Schottky plots obtained from the measured impedances of anodically passivating amorphous and polycrystalline TiO_2 films including multiple donor levels. The passivating amorphous TiO_2 films were prepared on titanium in 0.5 M H_2SO_4 solution galvanostatically at $2\,mA\,cm^{-2}$ at formation potentials of 2, 3 and 5 V/SCE, and the polycrystalline films at $5\,mA\,cm^{-2}$ at potentials of 20 and 30 V/SCE. The analysis was made by obtaining a numerical solution to a modified Mott-Schottky equation by using the Euler method. Based upon the analysis, the applied potential dependence of the donor distribution across the amorphous and polycrystalline TiO_2 films was determined for various film thicknesses and measuring frequencies. Ionized donor concentration increases with increasing applied potential, regardless of film thickness and measuring frequency. The thinner film and the lower measuring frequency enhance the donor concentration. It is suggested from the analysis of the nonlinear Mott-Schottky plots that the applied potential dependence of the donor distribution is attributable to the presence of multiple donor levels and that the donor concentration as a function of applied potential is definitely determined by the film thickness and measuring frequency.

1. Introduction

Donor distribution across anodically passivating TiO_2 films is of great importance in determining the overall efficiency of photoelectrochemical cells involving TiO_2 films as photoanodes [1, 2]. According to recent work [1–4], analysis of linear Mott-Schottky plots usually permits determination of a uniform donor distribution across a passivating TiO_2 film. In order to employ the linear analysis, the following condition is necessary: namely, the TiO_2 film specimen should be not amorphous or polycrystalline, but a single crystal semiconductor including a single donor level. Thus it may not be extended to an amorphous or polycrystalline thin TiO_2 film including multiple donor levels which cause a deviation from the linear Mott-Schottky plot.

Dean and Stimming [5] theoretically modified the linear Mott-Schottky relation in order to analyse the nonlinear Mott-Schottky plot by assuming the existence of multiple donor levels in any semiconductor. They assumed that the multiple donor levels are completely ionized one after another, suggesting that the nonlinear Mott-Schottky plot consists of two or more linear portions with different slopes. However they did not take into account the change of instantaneous slope in the Mott-Schottky plot and therefore the applied potential caused by the multiple donor levels.

Further, the nonlinear Mott-Schottky plots of the amorphous and polycrystalline TiO_2 films do not show a consistent behaviour for various film thicknesses and measuring frequencies. Thus it seems that the variation of the donor concentration with applied potential depends on the film thickness and measuring frequency.

The present work is aimed at making a numerical analysis of nonlinear Mott-Schottky plots obtained from amorphous and polycrystalline TiO_2 films by using the Euler method [6]. For this purpose a.c. impedance was measured as a function of applied potential for various film thicknesses and measuring frequencies.

2. Experimental details

Specimen preparation and impedance measurements were made at 300 K in a flat cell (EG&G Model KO 235) which had an exposed surface area of $1\,cm^2$. A platinum foil and a saturated calomel electrode were used as the counter electrode and reference electrode, respectively.

The passivated titanium electrode used as a working electrode was prepared from titanium foil of 99.99% purity (Alfa Products). The titanium specimen was etched in a 1:4:5 mixture of HF (48%), HNO_3 (65%) and distilled water. The anodically passivating amorphphous TiO_2 films were prepared galvanostatically at $2\,mA\,cm^{-2}$ in 0.5 M H_2SO_4 solution at formation potentials of 2, 3 and 5 V/SCE and the polycrystalline films at $5\,mA\,cm^{-2}$ at potentials of 20 and 30 V/SCE.

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The corresponding amorphous film thicknesses were measured to be 16, 20 and 23 nm, and the corresponding polycrystalline film thicknesses to be 62 and 83 nm, respectively, with an ellipsometer (Gaertner Scientific Corp.) at a beam wavelength of 632 nm. The amorphous and polycrystalline structures of passivating TiO_2 films were substantiated by using transmission electron microscopic (JEOL Model 2000EX) diffraction analysis. The presence of the multiple donor levels in the band gap of the passivating amorphous TiO_2 films has been confirmed by X-ray photoelectron spectroscopy (XPS).

The impedance measurements were performed on the TiO_2 films in an aqueous 0.5 M NaOH solution with a two-phase lock-in amplifier (EG&G Model 5208) and a potentiostat (EG&G Model 273) by superimposing an a.c. voltage of 5 mV amplitude on a d.c. potential over the frequency range of 5 to 10^4 Hz. The d.c. potential ranged between -0.8 and 1.2 V/SCE. The NaOH solution used as electrolyte was previously deaerated by bubbling with purified nitrogen.

3. Approach to analysis of nonlinear Mott-Schottky plot

In general, a uniform donor concentration in n-type passivating TiO_2 films including a single donor level has been determined from the linear slope of C^{-2} against V plot by employing the following Mott-Schottky equation [1–4]

$$C^{-2} = [2/(qNK\varepsilon_0 A^2)](V - V_{\mathrm{fb}} - kT/q) \qquad (1)$$

where C is the space charge capacitance of the semiconductor, q the electronic charge, N the donor concentration, K the relative dielectric constant, ε_0 the permittivity of free space, A the area of specimen, V the applied potential, V_{fb} the flatband potential, k the Boltzmann constant and T is the absolute temperature. The linear slope implies the absence of nonuniform donor concentration and/or multiple donor levels. Actually the slope of Mott-Schottky plot becomes nonlinear, when the concentration of the single donor level varies with distance into the semiconductor [7]. The instantaneous slope of the Mott-Schottky plot is expressed as follows.

$$\mathrm{d}C^{-2}/\mathrm{d}V = 2/[qN(V)K\varepsilon_0 A^2] \qquad (2)$$

where $\mathrm{d}C^{-2}/\mathrm{d}V$ is the instantaneous slope and $N(V)$ is the donor concentration at a given applied potential, V. Thus, by measuring the instantaneous slope, the ionized donor concentration in the TiO_2 film can be determined.

The nonlinear slope also results due to the presence of multiple donor levels in amorphous and polycrystalline TiO_2 films. In this case, of such multiple donor levels, only the levels with a higher energy than the Fermi level at a given applied potential are simultaneously ionized and contribute to an increase in the capacitance of the amorphous and polycrystalline TiO_2 films. Increasing the applied potential lowers the Fermi level. Consequently, the donor concentration depends upon the applied potential, producing a nonlinear slope in the Mott-Schottky plot. In other words, it is possible to quantitatively obtain the change of the donor concentration with applied potential from analysis of the nonlinear slope.

The modified Mott-Schottky relation has been theoretically suggested by Dean and Stimming [5]. This is given by

$$\begin{aligned}\mathrm{d}C^{-2}/\mathrm{d}V = {} & \{2/[qN(V)K\varepsilon_0 A^2]\} \\ & \times \{1 - qK\varepsilon_0 A^2 C^{-2}[\mathrm{d}N(V)/\mathrm{d}V]\} \qquad (3)\end{aligned}$$

where $N(V)$ represents a concentration of ionized multiple donors at an applied potential, V. Equation 3 is provided for calculation of the concentrations of some levels ionized at a given applied potential more anodic than the flatband potential, while Equation 2 is for determination of the uniform distribution of a single donor level completely ionized at the flatband potential. In Equation 3, each concentration of any level is assumed to be uniform across the TiO_2 films. It is noted that Equation 3 reduces to Equation 1 if the donors are uniformly distributed only over one level, i.e. the term $\mathrm{d}N(V)/\mathrm{d}V$ is negligibly small.

In the present work, we obtained a numerical solution to Equation 3 by using the Euler method in order to approximately determine $N(V)$. The numerical solution is given by

$$\begin{aligned}N(V_{i+1}) = {} & N(V_i)[1 - (\Delta V/2C_i^{-2})(\Delta C^{-2}/\Delta V)|_{V=V_i}] \\ & + \Delta V/(qK\varepsilon_0 A^2 C_i^{-2}) \qquad (4)\end{aligned}$$

where $N(V_{i+1})$ is the donor concentration at an applied potential, V_{i+1} and ΔV is the constant applied potential increment (see Appendix).

4. Results and discussion

In order to identify the amorphous and polycrystalline structures of the passivating TiO_2 films, we analysed the TEM diffraction patterns. Figure 1 presents the TEM diffraction patterns obtained from the TiO_2 films prepared at formation potentials of 5, 20 and 30 V/SCE. The 5 V/SCE passive film is in an amorphous state, but the 20 V/SCE and 30 V/SCE passive films show polycrystalline structures. The 2 V/SCE and 3 V/SCE passive films as well as the 5 V/SCE passive film possess amorphous structures, as expected since these films are thinner than the 5 V/SCE film.

Figure 2 shows the XPS spectra of valence band electrons in the amorphous TiO_2 films. Since these spectra in general reflect closely the density of states occupied by the valence band electrons, it is indicated by Fig. 2 that the donor levels are continuously distributed above the valence band. It is well known that oxygen vacancies in the TiO_2 film act as electron donors [1, 4]. So, the multiple donor levels here may be regarded as originating from non-homogeneous states of the valence band electrons which the oxygen

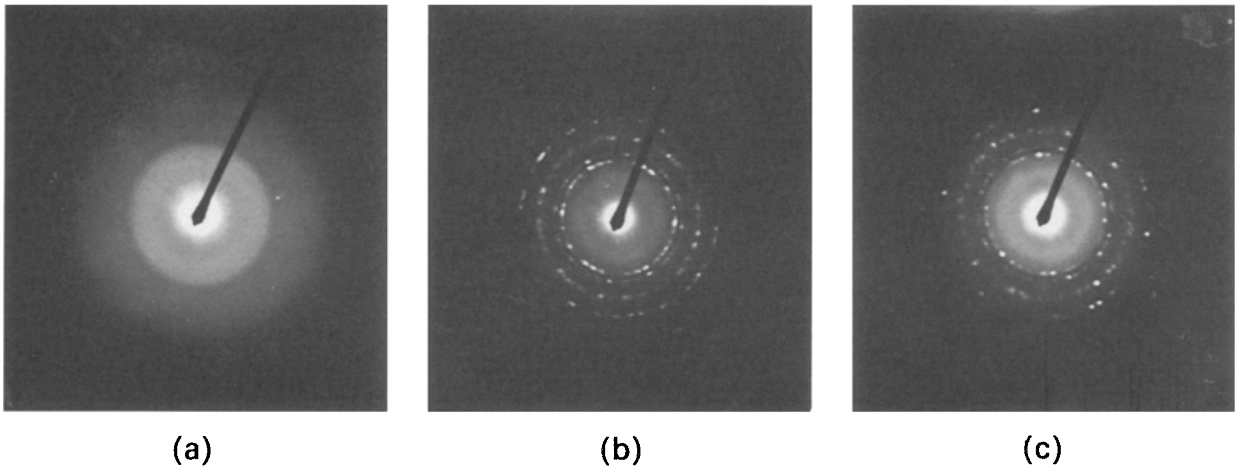

Fig. 1. TEM diffraction patterns obtained from (a) 5, (b) 20, (c) 30 V/SCE passivating TiO_2 films.

vacancies donate, due to the amorphous character of the film.

Figures 3 and 4 present the nonlinear Mott-Schottky plots obtained from the TiO_2 films including the multiple donor levels for various film thicknesses and measuring frequencies, respectively. The instantaneous slope gradually decreases with increasing applied potential, regardless of film thickness and measuring frequency. The gradual decrease of the slope suggests a change of the donor concentration with applied potential. The change is attributable to ionization of the multiple donor levels depending upon applied potential. At a given measuring frequency, the thicker the film, the stronger the influence of applied potential on the Mott-Schottky slope, and at a given film thickness, the lower the measuring frequency, the weaker the potential dependence of the Mott-Schottky slope becomes. From these results, it is expected that the donor concentration as a function of applied potential is definitely determined by the film thickness and measuring frequency.

From the analysis of the nonlinear slopes on the basis of the numerical solution (4), the donor concentration was obtained as a function of applied potential for the TiO_2 films of different thicknesses and is demonstrated in Fig. 5. The donor concentration increases with increasing applied potential for all the films. The increase of the donor concentration with applied potential is interpreted as follows. Some of the multiple donor levels are not yet ionized at an applied potential, V, and as the higher potential is applied, a larger number of donor levels become ionized. The increase of the donor concentration with decreasing film thickness at a given applied potential arises from the observation that the thinner film is more highly disordered [1] and hence has a higher concentration of multiple donor levels.

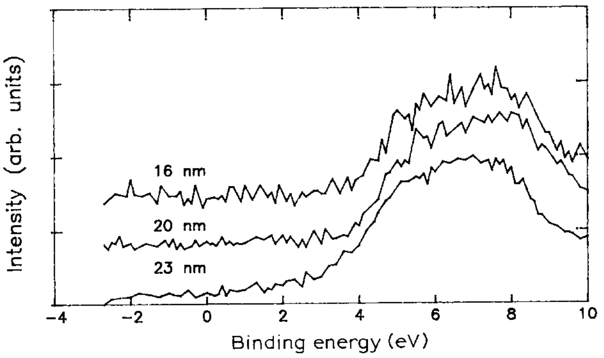

Fig. 2. Valence band spectra obtained from the amorphous TiO_2 films with different thicknesses.

From the same numerical analysis, the donor concentration was also determined as a function of applied potential for various measuring frequencies and is shown in Fig. 6. At a given measuring frequency, the donor concentration increased with increasing applied potential. The higher donor concentration was obtained for the lower measuring frequency at a given applied potential. Since donor levels respond slowly to the applied alternating potential, the lower measuring frequency validates the emission of electrons from the donor levels.

The analysis performed on the amorphous TiO_2 films can also be applied to polycrystalline films with multiple donor levels originating from grain boundaries, dislocations and deep levels. Fig. 7 presents

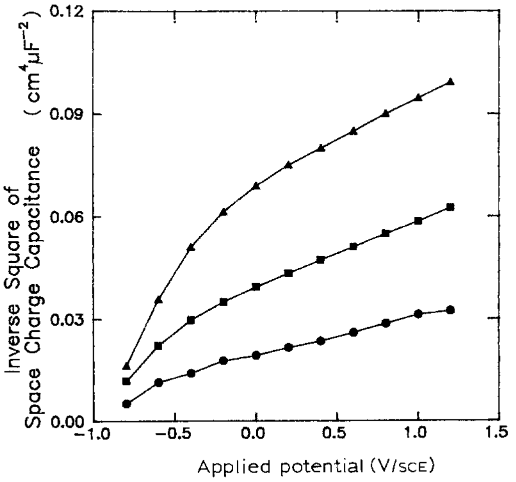

Fig. 3. Mott-Schottky plots obtained from the amorphous TiO_2 films with different thicknesses. Capacitance was measured at 158 Hz. Thickness: (●) 16, (■) 20 and (▲) 23 nm.

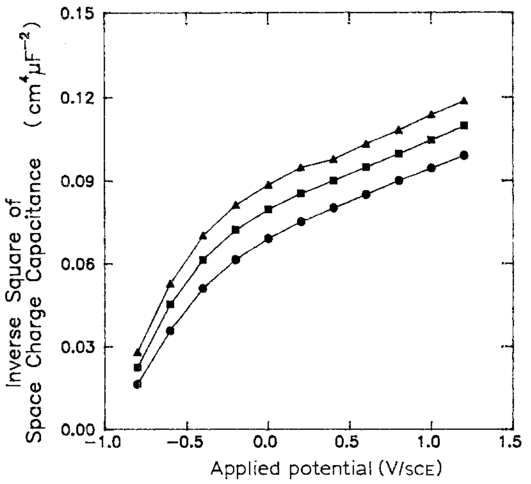

Fig. 4. Mott-Schottky plots obtained from the amorphous TiO_2 film with a thickness of 23 nm. Capacitance was measured at (●) 158, (■) 1000 and (▲) 1580 Hz.

nonlinear Mott-Schottky plots caused by the multiple donor levels. The result of the analysis on the polycrystalline TiO_2 films is demonstrated in Fig. 8. The average ionized donor concentration increases with increasing applied potential, irrespective of film thickness. This result is reasonable, considering the facts that ionization of deep donor levels and emission of electrons trapped deep at grain boundaries and dislocations require higher applied potentials. The lower donor concentration in the thicker film is most likely attributable to an increase of crystallinity.

5. Conclusions

Numerical analysis of nonlinear Mott-Schottky plots from amorphous and polycrystalline TiO_2 films was carried out as a function of applied potential for various thicknesses and measuring frequencies. The analysis was provided by numerical solution to the modified Mott-Schottky relation which is available only for a semiconductor including multiple donor levels. From the analysis of the nonlinear Mott-Schottky plots it is possible to obtain the continuous variation of the ionized donor concentration with

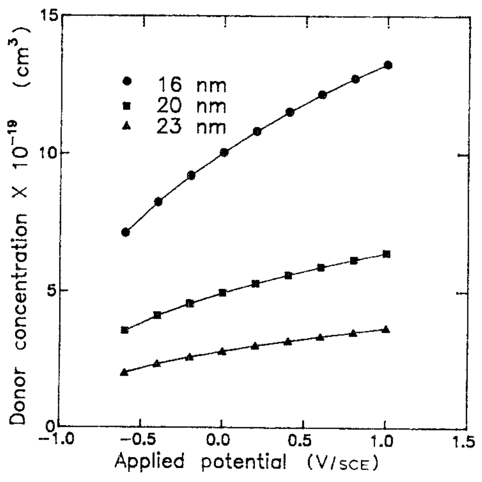

Fig. 5. Plot of donor concentration against applied potential, measured on the amorphous TiO_2 films with different thicknesses at a frequency of 158 Hz. Thickness: (●) 16, (■) 20 and (▲) 23 nm.

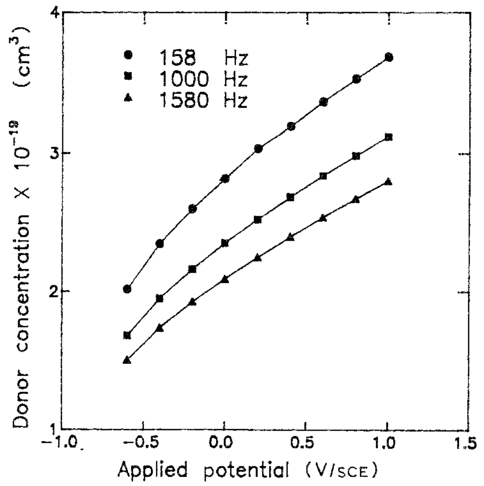

Fig. 6. Plot of donor concentration against applied potential, measured on the amorphous TiO_2 film with a thickness of 23 nm at frequencies of (●) 158, (■) 1000 and (▲) 1580 Hz.

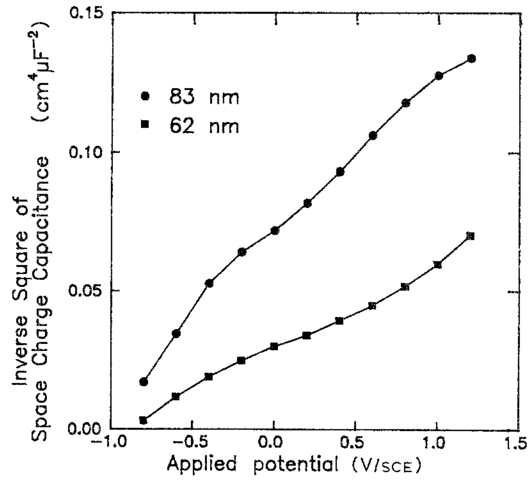

Fig. 7. Mott-Schottky plots obtained from the polycrystalline TiO_2 films of thickness (●) 83 and (■) 62 nm. Capacitance was measured at 1580 Hz.

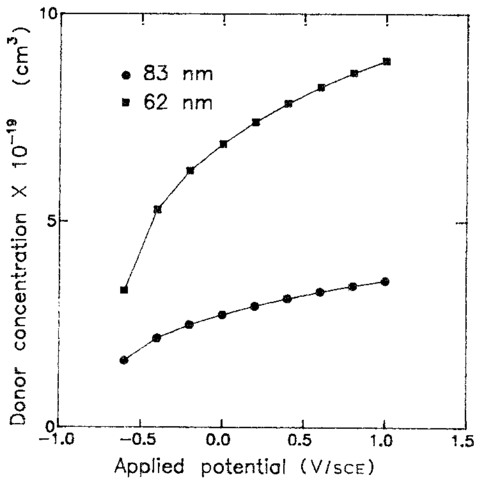

Fig. 8. Plot of donor concentration against applied potential, measured on the polycrystalline TiO_2 films of thickness (●) 83 and (■) 62 nm, at a frequency of 1580 Hz.

applied potential. The donor concentration increased appreciably with increasing applied potential at constant film thickness and measuring frequency. As film thickness or measuring frequency was decreased for a given applied potential, the donor concentration increased. This suggests that the variation of the donor concentraiton with applied potential is definitely determined by the film thickness and measuring frequency.

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Appendix

Numerical solution to Equation 3 by the Euler method.

The Euler method is described by

$$V(V_{i+1}) = N(V_i) + \Delta V \cdot f[V_i, N(V_i)] \qquad \text{(A1)}$$

This method was derived by using $[N(V_{i+1}) - N(V_i)]/\Delta V$ as an approximation to $\mathrm{d}N(V)/\mathrm{d}V$ expressed in Equation 3. For the differential Equation 3, the Euler equation becomes the difference equation

$$\begin{aligned} N(V_{i+1}) &= N(V_i)[1 - (\Delta V/2C_i^{-2})(\Delta C^{-2}/\Delta V)|_{V=V_i}] \\ &\quad + \Delta V/(qK\varepsilon_0 A^2 C_i^{-2}) \qquad \text{(A2)} \end{aligned}$$

where $\Delta V = V_{i+1} - V_i = V_i - V_{i-1} = \cdots$
It thus follows that

$$\begin{aligned} N(V_1) &= N(V_0)[1 - (\Delta V/2C_0^{-2}) \\ &\quad \times (\Delta C^{-2}/\Delta V)|_{V=V_0}] \\ &\quad + \Delta V/(qK\varepsilon_0 A^2 C_0^{-2}) \\ N(V_2) &= N(V_1)[1 - (\Delta V/2C_1^{-2}) \\ &\quad \times (\Delta C^{-2}/\Delta V)|_{\mathrm{V}=\mathrm{V}_1}] \qquad \text{(A3)} \\ &\quad + \Delta V/(qK\varepsilon_0 A^2 C_1^{-2}) \\ N(V_3) &= N(V_2)[1 - (\Delta V/2C_2^{-2}) \\ &\quad \times (\Delta C^{-2}/\Delta V)|_{V=V_2}] \\ &\quad + \Delta V/(qK\varepsilon_0 A^2 C_2^{-2}) \end{aligned}$$

The subscript i of Equation A1 refers to discrete applied potentials and a higher value of i represents more anodic potential. If the values of C_i are measured at a given applied potential and the initial value $N(V_0)$ and ΔV are given in Equation A2, $N(V_i)$ can be calculated from Equation A3 at any applied potential, V_i.