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Determination of energy distribution of donor levels in anodically passivating TiO_2 film

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Abstract

The present work is concerned with determination of energy distribution of donor levels by analysing a.c. impedance response from the anodically passivating TiO_2 films, based upon a new numerical method. The fresh and halide ion-incorporated anodic TiO_2 films were galvanostatically prepared on titanium substrate at 10 mA cm^{-2} to a formation potential of 50 V in deaerated 0.5 M H_2SO_4 solution and deaerated 0.5 M H_2SO_4 solution containing 0.5 M of Cl^- or Br^- respectively. Both a.c. impedance and photocurrent spectra were measured from the fresh and halide ion-doped anodic TiO_2 films to quantitatively determine the frequency dependence of donor concentration and energy distribution of deep donors formed by the halide ions. The new numerical method analysing the frequency dependence of donor concentration was proposed to determine the energy distribution of donor levels in the fresh and halide ion-doped anodic TiO_2 films. From the analysis of a.c. impedance response on the basis of the proposed new numerical method, it was suggested that donor levels are distributed continuously in the energy range of 0.55 to 0.67 eV below the conduction band edge. In addition, it was concluded that the donor concentration is reduced by the halide ion incorporation into the fresh anodic TiO_2 films in the measuring frequency range of 10 to 10^3 Hz, suggesting that the doped halide ions occupy oxygen vacancy sites and simultaneously form deep donor levels in the band gap of the anodic TiO_2 films.

Keywords: Energy distribution of donor levels; A.c. impedance; Passivation; Halide ion incorporation; Frequency dependence of donor concentration

1. Introduction

It is generally known that TiO_2 film is an n-type semiconductor in that oxygen vacancies play the role of donor [1–3]. Lee and Pyun [4] reported that the anodically passivating TiO_2 film includes multiple donor levels in the band gap from the analysis of modified Mott–Schottky relationship by using the Euler method. They qualitatively confirmed the presence of multiple donor levels over the wide energy range in the band gap by using the Euler method; however, they could not quantitatively determine the energy distribution of multiple donor levels in the anodic TiO_2 film.

Based upon the fact that the characteristic relaxation time is needed for ionisation of each donor, it is possible to determine the energy distribution of donor levels in the band gap rather quantitatively by analysing the frequency dependence of donor concentration within a limited measuring frequency range.

The present work is aimed at quantitatively determining the energy distribution of donor levels in the band gap of the fresh and halide ion-doped anodic TiO_2 films. For this purpose, the frequency dependence of donor concentration obtained from a.c. impedance measurement was analysed by using the proposed numerical method. The results of a.c. impedance response, analysed on the basis of proposed numerical method, were supplemented by those of photocurrent spectra.

2. Experimental details

The anodically passivating TiO_2 film used as a working electrode was prepared from titanium plate of 99.0% purity (Aldrich product). The titanium substrate was ground successively with SiC papers (grades 220,

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400, 600, 800 and 1200) and then finally polished with 0.3 μm Al_2O_3 powder. The fresh and halide ion-incorporated anodic TiO_2 films were galvanostatically prepared on the titanium substrate at 10 mA cm^{-2} to a formation potential of 50 V in deaerated 0.5 M H_2SO_4 solution and deaerated 0.5 M H_2SO_4 solution containing 0.5 M of Cl^- or Br^- respectively. It was assumed that the film thickness (approximately 100 nm) was not changed by the halide ion incorporation into the anodic TiO_2 film. A platinum net and a saturated calomel electrode (SCE) were respectively used as the counter and reference electrodes.

The a.c. impedance measurements were performed on the fresh and halide ion-doped anodic TiO_2 film specimens in deaerated 0.1 M NaOH solution with an impedance spectrum analyser (Zahner IM5d) by superimposing an a.c. voltage of 10 mV amplitude on a d.c. potential over the frequency range of 1 to 10^4 Hz. The d.c. potentials ranged between −0.6 and 0 V (SCE).

Photocurrents were measured as a function of incident light wavelength on the fresh and halide ion-doped anodic TiO_2 film specimens with a potentiostat (Wenking Model LT-78) connected to an x–t recorder (Soltec Model 1242) in deaerated 0.1 M NaOH solution. The incident light wavelength was varied from 700 to 2000 nm at a constant applied anodic potential of 1.0 V (SCE). Quartz glass was used as a window in the photoelectrochemical cell. The anodic TiO_2 films were illuminated with a 200 W Hg lamp (Oriel Model 66028), followed by a monochromator (Thermo Jarrel Ash Model 82-477).

Secondary ion depth profilings were performed on the halide ion-incorporated anodic TiO_2 films with a secondary ion mass spectrometer (SIMS, Perkin Elmer PHI 6300). Primary ion, beam voltage, beam current and raster size were Cs^+, 5 keV, 480 nA and 500 μm × 500 μm respectively.

3. New approach to determination of energy distribution of donor levels in the n-type semiconductor

For a crystalline n-type semiconductor with M discrete donor levels, the charge density ρ can be expressed by [5]

$$\rho = q\left(\sum_{i=1}^{M} N_{d_i}\{1 + \exp[(E_f - E_{d_i} - qV)/kT]\}^{-1} - N_c \exp[(E_f - E_c - qV)/kT]\right) \qquad (1)$$

where q represents the electronic charge; N_{d_i} is the donor concentration at ith energy level in the case that occupancy probability is unity; E_f is the Fermi level; E_{d_i} is the ith donor level; V is applied potential; k is the Boltzmann constant; T is the absolute temperature; N_c is the effective density of states in the conduction band and E_c is the energy of conduction band edge. In order that a donor at energy level E_{d_i} donates an electron to the conduction band, the activation energy $E_c - E_{d_i}$ should be overcome. A relaxation time τ_i is needed for ionisation of a donor at energy level E_{d_i} as given by [6]

$$\tau_i = \tau_0 \exp[(E_c - E_{d_i})/kT] \qquad (2)$$

where τ_0 is the lattice vibration time. As the relaxation time τ_i is the reciprocal of relaxation angular frequency ω_i, Eq. (2) can be presented as

$$\omega_i = \omega_0 \exp[(E_{d_i} - E_c)/kT] \qquad (3)$$

As the measuring angular frequency ω changes, e.g for ω equal to or less than the relaxation frequency ω_i, the donor at energy level E_{d_i} ionises, whereas it does not ionise for $\omega > \omega_i$. If a d.c. potential V and a measuring angular frequency ω_j are given, the total charge density $\rho^V_{\omega_j}$ of the donor ionising for $\omega_j \le \omega_i$ can be presented as

$$\rho^V_{\omega_j} = \rho^V_{\omega_{j+1}} + \Delta\rho^V_{\omega_j} \qquad (4)$$

with $\rho^V_{\omega_j} = \rho(V + \Delta V, \omega_j) - \rho(V - \Delta V, \omega_j)$ and $\omega_{j+1} > \omega_j$. $\rho^V_{\omega_j}$ consists of the summation of total charge density $\rho^V_{\omega_{j+1}}$ of the donor ionising for $\omega_{j+1} \le \omega_i$ and charge density fluctuation $\Delta\rho^V_{\omega_j}$ by the potential oscillation ΔV at the measuring frequency ω_j.

It is very convenient to express $\rho^V_{\omega_j}$ in terms of only $\Delta\rho^V_{\omega_j}$ to determine the energy distribution of donor levels from the measured frequency dependence of $\rho^V_{\omega_j}$. Considering a semiconductor having only a single donor level with relaxation frequency ω_i, on condition that $\omega_j \le \omega_i < \omega_{j+1}$, Eq. (4) is conveniently reduced to

$$\rho^V_{\omega_j} = [\rho(V + \Delta V, \omega_j) - \rho(V - \Delta V, \omega_j)] \qquad (5)$$

with the assumption that $\rho^V_{\omega_{j+1}} = 0$.

By substituting Eq. (1) into Eq. (5), one obtains $\Delta\rho^V_{\omega_j}$ as

$$\Delta\rho^V_{\omega_j} = qN_{d_i}[(1 + \exp\{[E_f - E_{d_i} - q(V + \Delta V)]/kT\})^{-1} - (1 + \exp\{[E_f - E_{d_i} - q(V - \Delta V)]/kT\})^{-1}] - AqN_c \exp[(E_f - E_c - qV)/kT] \qquad (6)$$

by using $A = \exp(-q\Delta V/kT) - \exp(q\Delta V/kT)$ which is constant at a given ΔV and T.

In the case of a semiconductor having multiple donor levels E_{d_i}, the relaxation frequencies ω_i necessary for ionisation of donors are distributed corresponding to the energy distribution of donor levels. It is assumed that each donor level is uniformly distributed throughout the semiconductor. If a d.c. potential V and a measuring angular frequency ω_j are given, the donor at each energy level ionises for a measuring frequency ω_j equal to or less than the relaxation frequency ω_i. Then Eq. (5) is conveniently extended to give Eq. (7), which is expressed in the summation form of the charge density fluctuation at each ω_i.

$$\rho^V_{\omega_j} = \sum_{i=\infty}^{j} [\rho(V + \Delta V, \omega_i) - \rho(V - \Delta V, \omega_i)] \qquad (7)$$

with $\omega_\infty > \omega_{\infty-1} > \cdots > \omega_{j+1} > \omega_j$.

$\rho^V_{\omega_j}$ can be regarded as the donor concentration N_d which can be determined from the instantaneous slope of the measured non-linear inverse-square capacitance C^{-2} vs. applied potential V plot (Mott–Schottky plot) at a given applied potential V and a measuring angular frequency ω_j. From the experimentally determined measuring frequency dependence of the absolute value of N_d on the basis of Eq. (7), one can obtain the ratio of the N_d increment to the decrement in unit logarithmic frequency $(\omega_j/2\pi)$ as a function of $\log(\omega_j/2\pi)$ representing the energy spectra of donor levels.

In contrast, the analysis of the modified Mott–Schottky relationship using the Euler method proposed by Lee and Pyun [4] accounts for the presence of multiple donor levels in the anodic TiO_2 film, but does not quantitatively provide the energy distribution of multiple donor levels.

4. Results and discussion

Donor concentration in the fresh anodic TiO_2 film experimentally determined from the linear region (−0.6 to 0 V (SCE)) of the Mott–Schottky plot is presented in Fig. 1(a) as a function of measuring frequency $(\omega_j/2\pi)$. Energy level $E_c - E_d$, corresponding to measuring frequency range 10 to 10^3 Hz, ranges between about 0.55 to 0.67 eV, assuming that τ_0 is 10^{-13} s [7]. N_d increases almost linearly with decreasing logarithmic measuring frequency. The instantaneous rate of increase of donor concentration to log measuring frequency, $\Delta N_d/\log[\omega_j/(\omega_j - \Delta\omega)]$, is plotted against measuring frequency in Fig. 1(b). The concentration of newly ionising donor per unit logarithmic frequency is nearly constant as about 3.2×10^{17} cm^{-3} over the entire measuring frequency range. This indicates that donor levels are continuously distributed in this energy range (0.55 to 0.67 eV) below the conduction band edge. The neutral oxygen vacancy rather easily donates an electron to become a singly charged oxygen vacancy. The second ionisation of an oxygen vacancy results in a relatively deep donor level in the band gap [8]. Butler et al. [9] reported that a distribution of defect-related traps is observed to extend about 0.8 eV below the conduction band edge. Considering the energy necessary for ionisation of the oxygen vacancy, it seems that the donor levels distrib-

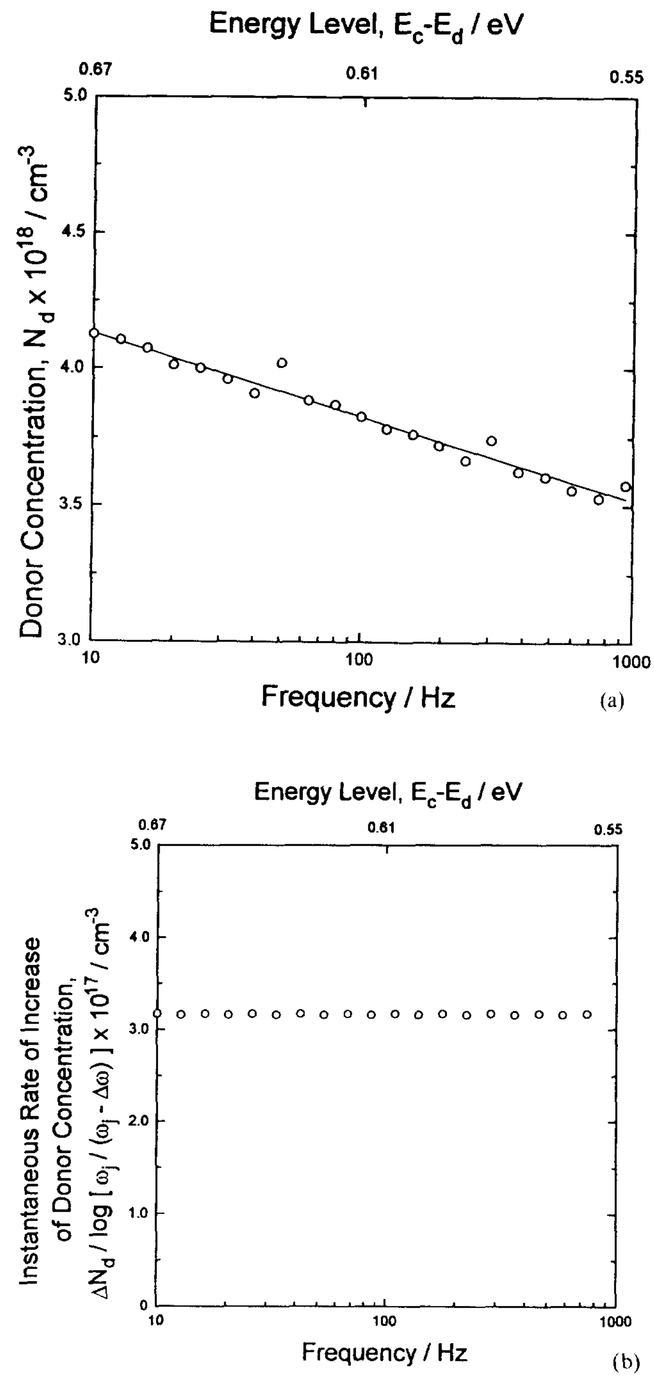

Fig. 1. Plot of (a) donor concentration N_d and (b) instantaneous rate of increase of donor concentration to log measuring frequency, ΔN_d $\log[\omega_j/(\omega_j - \Delta\omega)]$, against measuring frequency $\omega_j/2\pi$ for the fresh anodically passivating TiO_2 film in 0.1 M NaOH solution, measured in the applied potential range of −0.6 to 0 V (SCE). Circles (○) and solid line (———) represent measured data and fitted line respectively. The film was formed by application of a d.c. current density of 10 mA cm^{-2} to the formation voltage of 50 V in 0.5 M H_2SO_4 solution.

uted in this energy range are due to the second ionisation of the oxygen vacancy.

In order to determine the concentration profile of the incorporated halide ions within the anodic TiO_2 film, we analysed the results obtained from SIMS depth profilings. A logarithmic count ratio of halide ion to oxygen ion is presented as a function of sputter time in Fig. 2 for the various halide ions. Incorporated halide ion content increases in the order of $I^- < Br^- < Cl^-$. This indicates that smaller halide ions are more readily incorporated into the anodic TiO_2 film during the anodic oxidation. The Cl^- and Br^- ions incorporated into the anodic TiO_2 films are almost uniformly distributed across the entire films, except near surface region. In contrast, the incorporated I^- is relatively less-uniformly distributed over the film. Among the halide ion-incorporated films, Cl^- and Br^--doped films satisfy the above mentioned assumption that donor levels are uniformly distributed across the anodic TiO_2 film. Therefore, the new numerical approach already introduced in this work is appropriately applicable to determine the energy distribution of donor levels in the band gap of the Cl^-- and Br^--doped films.

Donor concentrations in the Cl^-- and Br^--doped anodic TiO_2 films experimentally determined from the linear region (−0.6 to 0 V (SCE)) of the Mott–Schottky plot are presented in Fig. 3(a) as a function of measuring frequency. Similar to the result of Fig. 1(a), N_d increases almost linearly with decreasing logarithmic measuring frequency. The instantaneous rate of increase of donor concentration to log measuring frequency, $\Delta N_d / \log[\omega_j/(\omega_j - \Delta\omega)]$, is plotted against measuring frequency in Fig. 3(b). The increments in concentration of newly ionising donor by Cl^- and Br^- incorporation remain constant for the Cl^-- and Br^--doped films at about 1.3×10^{17} and 3.0×10^{17} cm^{-3}

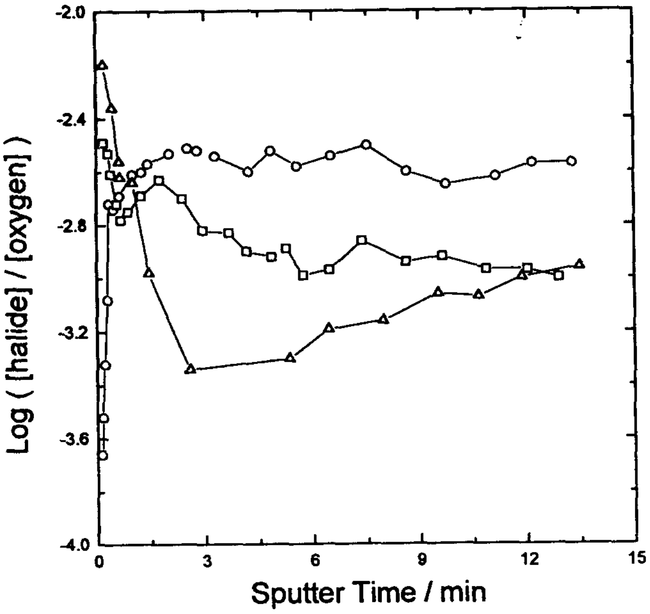

Fig. 2. Plot of logarithmic ratio of halide ion count to oxygen ion count versus sputter time for various halide ions of: ○, Cl^-; □, Br^-; △, I^-.

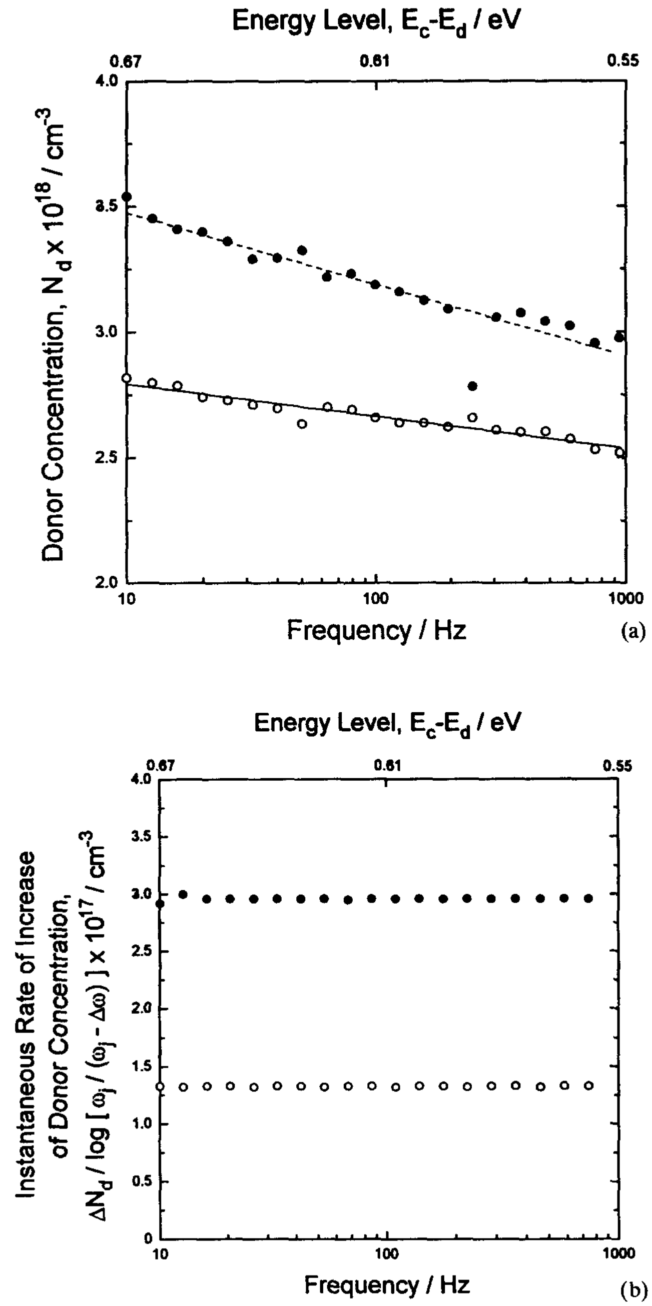

Fig. 3. Plot of (a) donor concentration N_d and (b) instantaneous rate of increase of donor concentration to log measuring frequency, ΔN_d $\log[\omega_j/(\omega_j - \Delta\omega)]$, against measuring frequency $\omega_j/2\pi$ for Cl^--doped (○) and Br^--doped (●) anodic 50 V-TiO_2 films in 0.1 M NaOH solution, measured in the applied potential range of −0.6 to 0 V (SCE). Solid line (———) and dotted line (– – –) represent fitted lines for the Cl^-- and Br^--doped anodic 50 V-TiO_2 films respectively. The films were formed by application of a d.c. current density of 10 mA cm^{-2} in 0.5 M H_2SO_4 solution containing 0.5 M of Cl^- or Br^-.

per unit logarithmic frequency respectively. These results indicate that donor levels are continuously distributed in this energy range below the conduction band edge.

Fig. 4(a) shows differences ($[N_d(\text{undoped}) - N_d(\text{doped})]$) between N_d in the fresh film and those in the Cl^-- and Br^--doped films as a function of measuring frequency. $[N_d(\text{undoped}) - N_d(\text{doped})]$ for the Cl^-- and Br^--doped films increases almost linearly with decreasing logarithmic measuring frequency investigated. $[N_d(\text{undoped}) - N_d(\text{doped})]$ for the Cl^--doped film is larger than that for the Br^--doped film, regardless of measuring frequency. N_d(doped) is smaller than N_d(undoped), even at frequencies higher than 10^3 Hz, indicating that incorporated halide ion decreases the concentration of donor ionising above 10^3 Hz (0.55 eV).

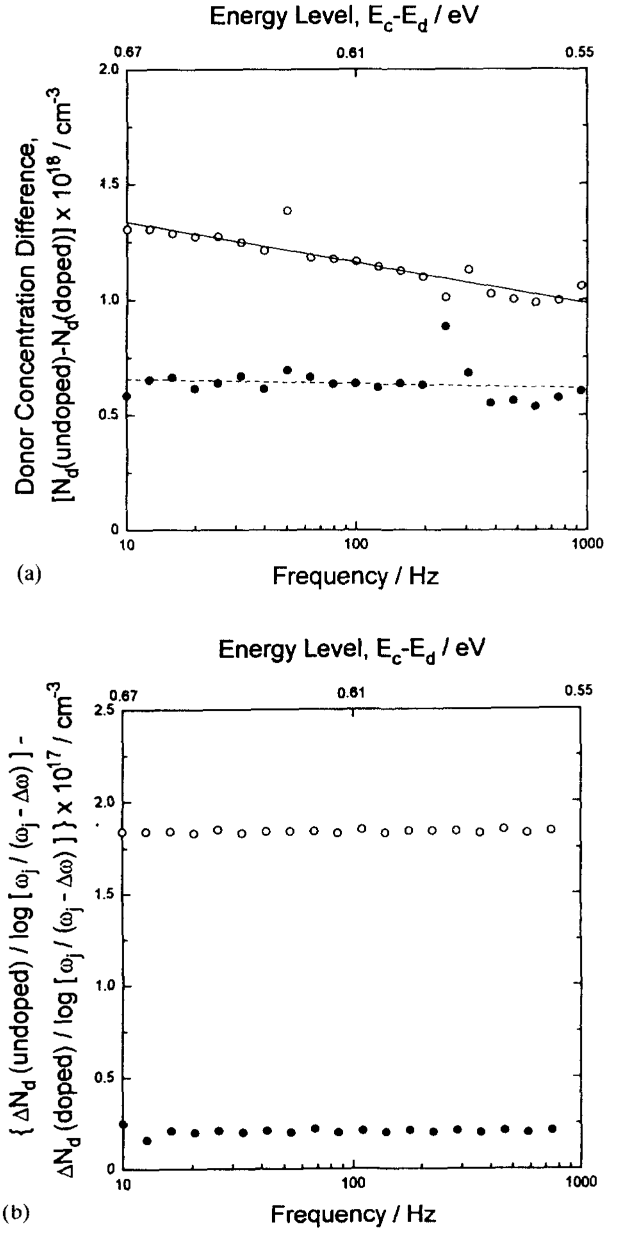

Fig. 4. Measuring frequency dependence of (a) difference between donor concentrations in the fresh anodic 50 V-TiO_2 film and Cl^--doped (○) or Br^--doped (●) anodic 50 V-TiO_2 film, ($[N_d(\text{undoped}) - N_d(\text{doped})]$), and (b) difference between instantaneous rates of increase of donor concentration to log measuring frequency, $\{\Delta N_d(\text{undoped})/\log[\omega_j/(\omega_j - \Delta\omega)]\} - \{\Delta N_d(\text{doped})/\log[\omega_j/(\omega_j - \Delta\omega)]\}$, for the fresh anodic 50 V-TiO_2 film and Cl^--doped (○) or Br^--doped (●) anodic 50 V-TiO_2 film. Solid line (———) and dotted line (- - -) represent fitted lines for Cl^-- and Br^--doped anodic 50 V-TiO_2 films respectively.

In order to investigate the effect of incorporated halide ion on the concentration of newly ionising donor per unit logarithmic frequency, the difference between instantaneous rates of increase of donor concentration by halide ion incorporation to log measuring frequency, $\{\Delta N_d(\text{undoped})/\log[\omega_j/(\omega_j - \Delta\omega)]\} - \{\Delta N_d(\text{doped})/\log[\omega_j/(\omega_j - \Delta\omega)]\}$, is considered. Fig. 4(b) shows $\{\Delta N_d(\text{undoped})/\log[\omega_j/(\omega_j - \Delta\omega)]\} - \{\Delta N_d(\text{doped})/\log[\omega_j/(\omega_j - \Delta\omega)]\}$ as a function of measuring frequency. The instantaneous rate of increase of donor concentration to log measuring frequency for the doped film is smaller than that for the undoped film over the entire frequency range. The decrements in donor concentration by Cl^- and Br^- incorporation remain nearly constant as about 1.9×10^{17} and 0.2×10^{17} cm^{-3} per unit logarithmic frequency respectively. This means that incorporated halide ion reduces the concentration of donor ionising per unit logarithmic frequency by a constant amount. The decrease of donor concentration by the halide ion incorporation can be accounted for in the following way.

A large strain could be induced by halide ion incorporation into the anodic TiO_2 film owing to the large ionic radius of halide ion. Hence, in order to relieve the strain, it is reasonable to regard that some incorporated halide ions tend to be located at oxygen vacancies and, moreover, the formation of oxygen vacancy is suppressed. It is suggested that halide ion occupies the oxygen vacancy ionising in this measuring frequency range as

$$X^- + \ddot{V}_O \rightleftharpoons \dot{X}_O \tag{8}$$

where X^-, V_O and X_O represent the halide ion, the oxygen vacancy and the incorporated halide ion respectively. It is expected that the halide ion incorporated by reaction (8) decreases the effective donor concentration and forms deep donor levels because the incorporated halide ion is very attractive to an electron; hence the ionisation energy of incorporated halide ion is large.

The absolute value of photocurrent density is rather ambiguous but it is possible to determine the energy levels formed by doped halide ion in the band gap from the location of the peak appearing in the relative photocurrent spectrum. The relative photocurrent

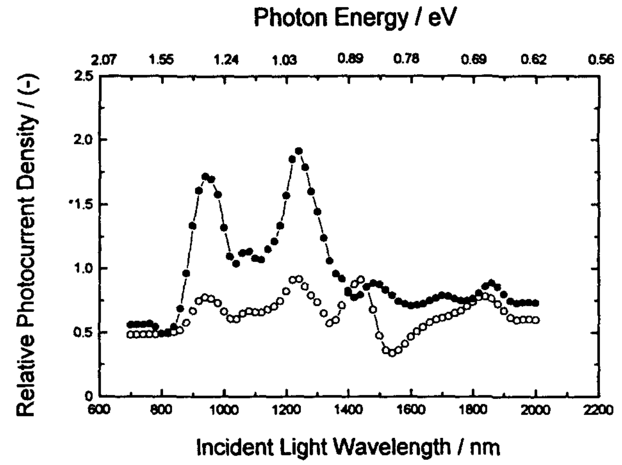

Fig. 5. Plot of relative photocurrent density vs. incident light wavelength and photon energy for the Cl^--doped (○) and Br^--doped (●) anodic 50 V-TiO_2 films in 0.1 M NaOH solution, measured at an applied potential of 1.0 V (SCE).

density (ratio of the photocurrent density of the halide ion-incorporated film to that of the fresh film) is presented in Fig. 5 as a function of incident light wavelength and photon energy. The photocurrent density is obtained by subtracting the dark current density from the measured photocurrent density. The mean value of the relative photocurrent densities for the Cl^-- and Br^--doped films in the photon energy range of 0.62 to 1.77 eV are about 0.7 and 0.9 respectively. The relative photocurrent spectrum for the Cl^--doped film shows several peaks at about 0.7, 0.85, 1.05 and 1.3 eV below the conduction band edge. That spectrum for the Br^--doped film shows two sharp peaks at 1.05 and 1.3 eV.

It is reported [10] that the photocurrent density decreases with decreasing donor concentration in the donor concentration and film thickness ranges investigated. The mean values of the relative photocurrent density less than unity for the Cl^-- and Br^--doped films seem to originate from the decrease of total donor concentration by the halide ion incorporation through the suggested reaction (8). The peaks appearing in the relative photocurrent spectra for the halide ion-incorporated films indicate the presence of the energy levels formed by the halide ions incorporated into the films. The complicated variation of relative photocurrent densities indicates that there are other reactions concerned with the production of deep donor levels as well as the proposed reaction (8). The reactions between incorporated halide ions and water molecules, hydroxyl ion and other impurities usually present in the anodic TiO_2 films may provide other sources of deep donor level formation.

5. Conclusions

A new numerical method for analysing the frequency dependence of donor concentration was proposed to quantitatively determine the energy distribution of donor levels in fresh and halide ion-doped anodic TiO_2 films. From the analysis of a.c. impedance spectra based upon the proposed new numerical method, it was suggested that donor levels in the fresh and halide ion-doped anodic TiO_2 films are continuously distributed in the energy range of 0.55 to 0.67 eV below the conduction band edge. Also, it was concluded that the donor concentration is reduced by the halide ion incorporation into the fresh anodic TiO_2 films in the measuring frequency range of 10 to 10^3 Hz, suggesting that the doped halide ions occupy oxygen vacancy sites and simultaneously form deep donor levels in the band gap of the anodic TiO_2 films.

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