

***I-V* and *C-V* Characteristics of Au/TiO₂ Schottky diodes**

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The electrical characteristics of Au/*n*-TiO₂ Schottky diodes have been studied using *I-V* and *C-V* measurements. TiO₂ samples with working face perpendicular to the *c* axis are reduced in a vacuum of 10⁻⁶ Torr at 800 °C for about 5 h and then quenched. The resistivities are in the range 20–30 Ω cm. The barrier heights deduced from *I-V* characteristics in agreement with the thermionic emission theory are in the range 0.87–0.94 eV. *C-V* data yield lower barrier heights and show a frequency dependence attributed to relaxation phenomena occurring in a disturbed layer near the surface. Comparison with results relative to Au/*n*-SrTiO₃ diodes shows that the barrier heights obey the Schottky model for these ionic semiconductors, confirming the role of the electron affinity in the band bending formation.

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I. INTRODUCTION

Photoelectrolysis of water as a new method for solar energy conversion initiated a growing interest for semiconductor electrodes in electrochemistry. In their pioneering work, Fujishima and Honda¹ demonstrated the feasibility of the photoelectrolysis of water using TiO₂ as photoanode. Unfortunately, due to the large bandgap ($E_g = 3$ eV), energy conversion efficiencies are too low (< 1%) to make TiO₂ a promising material. Mavroides *et al.*² show that SrTiO₃ ($E_g = 3.2$ eV) is also able to catalyse the decomposition of water and find external quantum efficiencies an order of magnitude higher than those obtained with TiO₂ in the same experimental conditions without bias voltage. These authors attribute the increase of the efficiencies to a larger band bending at the SrTiO₃ surface resulting from a lower electron affinity relative to that observed with TiO₂. Consequently, after Mavroides *et al.*, an ideal anode material for solar energy conversion by means of photoelectrolysis would have not only an energy gap adapted to the solar spectrum, but also a low electron affinity. The band bending produced at the semiconductor surface when the anode is immersed in an electrolyte is analogous to a Schottky barrier observed in the case of the metal-semiconductor contact. It has been verified that the barrier height ϕ_B on ionic semiconductors (SrTiO₃ for example) is strongly dependent on the metal work function ϕ_m following the Schottky model

$$\phi_B = \phi_m - \chi. \quad (1)$$

But it is not obvious that, for a given metal, ϕ_B varies with the electron affinity χ of ionic semiconductors as predicted by Eq. (1). Then, we propose to determine the barrier height of the Au/*n*-TiO₂ contact by classical *I-V* and *C-V* characteristics analysis. The comparison with the results of Neville and Mead³ relative to Au/*n*-SrTiO₃ diodes should verify the analogous behavior of the contacts between these ionic semiconductors and a metal or an electrolyte, and therefore confirm the hypothesis of Mavroides *et al.* based on the electron affinity for the choice of water photoelectrolysis materials.

II. EXPERIMENTAL

Rutile single crystals are used. The samples are cut into about 1 × 2 cm² by 2 mm thick and two sides chemically-mechanically polished to a final thickness of 250 μm, the largest faces being perpendicular to the *c* axis. The samples are then cleaned according to the following steps: ultrasonically degreased in detergent solution, rinsed in flowing deionized water and next in boiling methyl alcohol, and dried in N₂ flow. The slices are reduced in an adapted quartz crucible under a vacuum of 10⁻⁶ Torr at 800 °C for about 5 h. The samples are then quenched; the rapid decrease of the treatment temperature to the room temperature takes only a few minutes. Point defects, e.g., oxygen vacancies due to the reduction, act as donor centers and change the insulating rutile into a *n*-type semiconductor. The experimental conditions have been chosen in agreement with the results of Iguchi and Yajima⁴ to get a distribution of point defects approximately homogeneous throughout the specimen. The resistivities are measured at room temperature by four-probes method and are in the range 25 ± 5 Ω cm. Thereafter the Au/*n*-TiO₂ contacts are fabricated by gold evaporation through a Ni mask. The thickness of the Au film is approximately 5000 Å and the diodes are circular with areas of 2.8 × 10⁻³ cm².

The Au/*n*-TiO₂ diodes are evaluated using measurements of forward or reverse *I-V* characteristics and *C-V* characteristics at room temperature in a light-tight box to avoid effects of light-stimulated current.

In agreement with the standard thermionic emission theory (see for example Sze⁵), the barrier height ϕ_B can be deduced from the saturation current I_0 :

$$\phi_B = kT \ln(SA^*T^2/I_0), \quad (2)$$

where k is the Boltzmann constant, S is the area of the diode, and T is the absolute temperature. Assuming an effective mass m^* of the charge carriers in TiO₂ equal to 9 m_0 ,⁶ where m_0 is the free electron mass, the appropriate Richardson constant A^* is approximately 1100 A cm⁻² K⁻². The barrier height can be also deduced from the knowledge of the diffusion voltage V_D obtained from measurements of the vari-

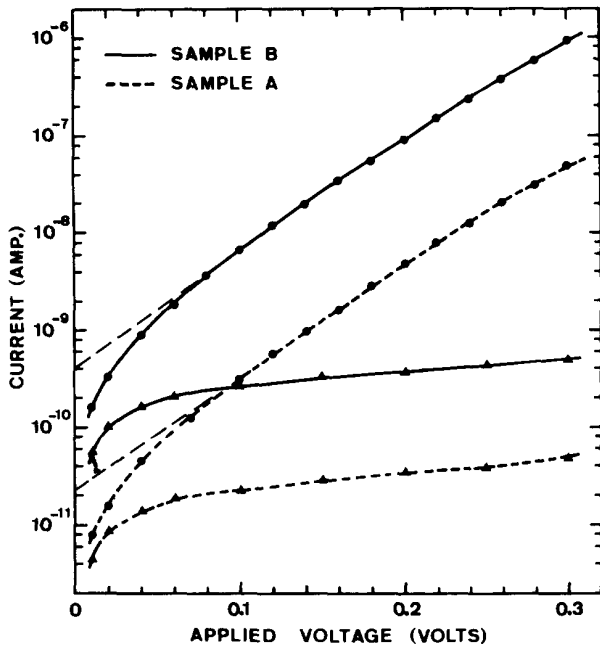


FIG. 1. Typical forward (●) and reverse (▲) I - V characteristics of two Au/TiO₂ diodes. Sample A: $n = 1.4$, $I_{0A} = 2.5 \times 10^{-11}$ A; Sample B: $n = 1.35$, $I_{0B} = 4 \times 10^{-10}$ A.

ation of the capacitance with applied voltage:

$$\phi_B = q(V_D + \delta n + kT/q), \quad (3)$$

where

$$\delta n = (kT/q) \ln(N_C/N_D).$$

N_D is the donor concentration and N_C is the effective density of states in the conduction band of TiO₂ ($\sim 7 \times 10^{20}$ cm⁻³ for $m^*/m_0 = 9$). The diode capacitance is measured with a General Radio 1615 A capacitance bridge. Measuring frequencies ranged from 100 to 10000 Hz.

III. RESULTS AND DISCUSSION

Forward and reverse current-voltage characteristics for two typical Au/ n -TiO₂ diodes are shown in Fig. 1. Some spread appears between the different measured diodes which can be due to the unhomogeneous reduction of the crystal.

The forward curves give an ideality factor equivalent to 1.4 for the sample A and 1.35 for the sample B. Therefore the current is predominantly thermionic and Eq. (2) is a good approximation to calculate the barrier height ϕ_B . The intercept currents $I_{0A} = 2.5 \times 10^{-11}$ A and $I_{0B} = 4 \times 10^{-10}$ A corresponding also to the saturation currents of reverse characteristic (for V superior to a few kT/q), give at room temperature calculated barrier heights equal to 0.94 eV and 0.87 eV for the diodes A and B, respectively.

Plots of C^{-2} versus V for the diode B is shown in Fig. 2. The differential capacitance varies linearly with applied voltage according to the Mott-Schottky relationship but is frequency dependent, plots corresponding to higher frequencies being situated above plots at lower frequency for a given voltage. Then it may be asked whether the usual expression relating the slope to the doping level N_D is valid

here:

$$\frac{dC^{-2}}{dV} = \frac{2}{S^2 q N_D \epsilon \epsilon_0},$$

where ϵ , ϵ_0 are, respectively, the permittivity of the free space and the dielectric constant for TiO₂ taken as⁶ 173 when the electric field is parallel to the c axis. The value of N_D extracted from the 10-kHz curve is approximately equal to 2×10^{17} cm⁻³. Assuming a mobility of⁷ 1 cm² V⁻¹ S⁻¹ the equivalent resistivity will be 30Ω cm, in agreement with the values previously determined by the four-point probe method (20 – 30Ω cm).

The Mott-Schottky plots, determined at different frequencies, converge to a common point V_D situated on the V axis. $V_D = 0.5$ V is the built-in voltage which allow us to calculate ϕ_B theoretically by the relation (3). Knowing the doping level $N_D = 2 \times 10^{17}$ cm⁻³ and assuming an effective density of states in the conduction band $N_C = 7 \times 10^{20}$ cm⁻³, the barrier height ϕ_B deduced from C - V measurements is 0.74 eV, in poor agreement with the value deduced from the I - V characteristics (0.87 eV). Recently, comments of Cardon and Gomes⁸ on the determination of the flat-band potential of a semiconductor in contact with a metal or an electrolyte from the C - V plot show that the experimental barrier height can deviate from ideality. Possible sources of deviation are listed by these authors; in particular points (3) and (4) of their paper, e.g., the presence of surface states interacting with the free carriers of the semiconductor and/or the existence of an insulating layer between the semiconductor and metal or electrolyte phase can have large effects on the capacitance and therefore on the flat-band potential. These are possible reasons to explain the discrepancy between the barrier heights deduced from I - V characteristics and those deduced from C - V characteristics.

The frequency-dependent C^{-2} vs V plot has been found by Laflere *et al.* in the case of a classical semiconductor, e.g., GaAs in contact with an electrolyte⁹ or a metal.¹⁰ TiO₂-electrolyte contacts, also present such characteristics as shown by Dutoit *et al.*^{11,12} Our work confirms that the frequency dependence of the capacitance is a true property of TiO₂. In

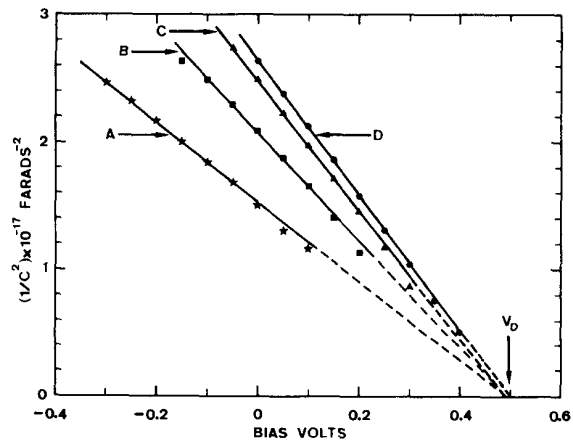


FIG. 2. Plot of $1/C^2$ vs V for sample B. A, 100 Hz; B, 1000 Hz; C, 5000 Hz; D, 10000 Hz; $V_D = 0.5$ V.

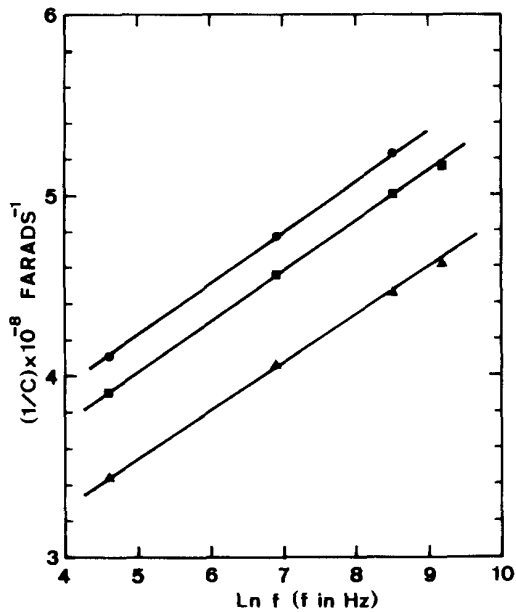


FIG. 3. Plot of C^{-1} vs $\ln f$ for the Au/TiO₂ diode. Sample B, Applied voltages: ●, 0.05 V; ■, 0 V; ▲, 0.1 V.

order to explain the frequency effects, Dutoit *et al.* assume that dielectric relaxation phenomena occur in a disturbed layer which is present near the surface extending more or less deeply into the crystal. Sculfort and Baticle¹³ also observe a frequency dependence of the impedance of the contact n -type Ga_xIn_{1-x}P/electrolyte attributed to dipole relaxation phenomena in the space charge layer of the semiconductor electrode, in relation to the surface etching and polishing.

Such a model interprets the linear C^{-1} vs $\ln f$ relation where f is the frequency. C^{-1} vs $\ln f$ plots are shown in Fig. 3 for the effect occurring in a layer on the semiconductor surface is valid in our case, the frequency behavior of the capacitance of TiO₂/Au contact being analogous to that of TiO₂/electrolyte interface, when the disturbed layer extends deeper than the depletion layer.

Knowing the barrier heights of the Au/ n -TiO₂ contact (0.9 eV) and of the Au/ n -SrTiO₃ diode (1.2 eV) determined by Neville and Mead,³ we can now verify the Schottky model for the two ionic semiconductors in contact with gold. On the basis of electron affinities values equal to 4 eV for TiO₂,¹⁴ 3.8 eV for SrTiO₃,² and of the gold work function measured in our laboratory (4.9 eV), and taking into account the currently accepted accuracy of these parameters and measured barrier heights (0.1–0.2 eV), present data are consistent with the original Schottky proposal, Eq. (1). The Schottky barrier on TiO₂ is lower than on SrTiO₃ and consequently, the mod-

el proposed by Mavroides *et al.*, taking into account the electron affinity of the semiconductor electrode for the choice of water photoelectrolysis materials, is confirmed by our experiments.

IV. CONCLUSION

Au films evaporated onto TiO₂ crystal reduced and quenched in vacuum, yield Schottky barrier heights of about 0.90 eV as deduced from I - V characteristics analysis. A frequency dependence of the Au/ n -TiO₂ diode capacitance is observed and attributed to dielectric relaxation phenomena in a disturbed layer near the surface as suggested by Dutoit *et al.* and depends on the nature of the surface preparation. The measured barrier height is consistent with the Schottky model of the contact between ionic semiconductor and metal, and confirms the importance of the electron affinity on the barrier or band-bending formation. The hypothesis of Mavroides *et al.* based on the electron affinity for the choice of water photoelectrolysis materials is confirmed, e.g., smaller is the electron affinity, greater is the band bending and higher is the efficiency of the solar conversion using semiconductors with ionic character, assuming the same collection length.

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