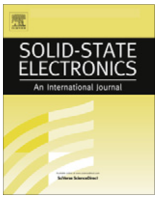
Solid-State Electronics 80 (2013) 142–151

Contents lists available at SciVerse ScienceDirect

Solid-State Electronics

journal homepage: www.elsevier.com/locate/sse



Effect of high current density on the admittance response of interface states in ultrathin MIS tunnel junctions

Christian Godet *, Alain-Bruno Fadjie-Djomkam, Soraya Ababou-Girard

Institut de Physique de Rennes, CNRS UMR 6251, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

ARTICLE INFO

Article history:
Received 12 March 2012
Received in revised form 26 September 2012
Accepted 11 October 2012
Available online 16 January 2013

The review of this paper was arranged by Prof. S. Cristoloveanu

Keywords:
Tunnel MIS diode
Organic monolayer
Electrical transport
Admittance
Interface states
Current density

ABSTRACT

The effect of a high current density on the measured admittance of ultrathin Metal–Insulator–Semiconductor (MIS) tunnel junctions is investigated to obtain a reliable energy distribution of the density, $D_S(E)$, of defects localized at the semiconductor interface. The behavior of admittance $Y(V, T, \omega)$ and current density $J(V, T)$ characteristics is illustrated by rectifying Hg//$C_{12}H_{25}$—Si junctions incorporating *n*-alkyl molecular layers (1.45 nm thick) covalently bonded to *n*-type Si(1 1 1). Modeling the forward bias admittance of a nonequilibrium tunnel junction reveals several regimes which can be observed either in $C(\omega \approx 0)$ vs. (J) plots of the low frequency capacitance over six decades in current or in $M''(\omega)$ plots of the electrical modulus over eight decades in frequency. At low current density, the response of interface states above mid-gap is unaffected and a good agreement is found between the interface states densities derived from the modeling of device response time $\tau_R(V)$ and from the low–high frequency capacitance method valid for thick MIS devices; the low defect density near mid-gap ($D_S < 10^{11}$ eV^{-1} cm^{-2}) results from a good passivation of dangling bonds at the $C_{12}H_{25}$—*n* Si interface. In the high current density regime ($J > 1$ mA cm^{-2}), the admittance depends strongly on both the density of localized states and the dc current density, so that the excess capacitance method overestimates D_S. For very high current densities ($J > 10$ mA cm^{-2}), the observation of a linear $C(\omega \approx 0)$ vs. (J) dependence could indicate some Fermi level pinning in a high interface density of states located near the Si conduction band. The temperature-independent excess capacitance $C(\omega \approx 0) - C(1\text{ MHz})$ observed at very small J, not predicted by the admittance model, is attributed to some dipolar relaxation in the molecular junction.

1. Introduction

The development of Metal–Insulator–Semiconductor (MIS) junctions with ultra-thin insulator ($d_T < 3$ nm) has stimulated the study of new insulating materials, such as saturated organic chains with a wide electronic band gap (≈7 eV) [1]. In the field of hybrid molecular–silicon junctions, alkyl-based devices have been investigated for fundamental studies of transport mechanisms (thermionic emission, tunneling, recombination) while applications are foreseen in the fields of solar cells and gate insulators [2,3]. Alkyl monolayers may form a well controlled interlayer for further assembly of nanoscale objects (molecules, nanoparticles, nanotubes) providing new functionalities to form original devices and circuit architectures [4–8].

Covalent binding of linear saturated (*n*-alkyl) chains to hydrogenated Si(1 1 1):H surfaces [9] forms robust molecular layers with a high coverage which play the role of a nanometer-thick tunnel barrier. Due to sterical constraints, the density of surface Si—H sites which are not grafted with alkyl molecules is larger than 4×10^{14} cm^{-2} (≈60% of surface Si atom density); however, the density of electrically active defects, D_S, remains relatively small, at least immediately after grafting, in the 1×10^{10} to 3×10^{11} eV^{-1} cm^{-2} range [10–15]. However, besides the problem of engineering a homogeneous and reliable top electrode in contact with a nanometer-thick molecular monolayer, a major issue in hybrid molecular–silicon junctions is the structural disorder which results from the irreversible grafting mechanism related to the strong covalent bonding; hence structural disorder probably induces some distribution of barrier heights for electrical transport and may explain the wide range of conductance values observed experimentally [16,17].

In metal/semiconductor (SC) junctions, the presence of interface states and of a thin insulating layer have been recognized as nonidealizing factors in the current–voltage (*I–V*) characteristics [18–21]. A number of methods based on *non-stationary* measurements have been developed for interface defect characterization in thick MIS diodes [22,23] and tentatively extended to MIS junctions with interfacial layers [24,25], ultrathin SiO_2 [19,26–29], and molecular insulator [3,14,15,30]. In the latter devices, frequency and temperature dependence of molecular MIS admittance

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* Corresponding author. Address: EPSI – IPR (Bât. 11C – Beaulieu), Université Rennes 1, 35042 Rennes, France. Tel.: +33 2 23 23 57 06; fax: +33 2 23 23 61 98.

E-mail address: christian.godet@univ-rennes1.fr (C. Godet).

0038-1101/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.sse.2012.10.012

brings valuable information to discriminate interface states response and dipolar relaxation effects [14,31–33].

MIS tunnel diodes are *nonequilibrium* devices due to the large current density flowing through the thin insulating layer (Fig. 1). It has been shown that, between 1 and 2 nm thick SiO_2, the quasi-static hypothesis progressively fails and a kinetic approach should be developed [34]; this effect is expected to occur at larger thickness values for an insulator with a lower tunnel barrier height. We must then calculate the position of the quasi-Fermi level at the interface, its value depending on the applied voltage, on the transmission coefficient of the barrier (i.e. essentially on the insulator thickness) and on the interface defects. The *non-stationary* transport properties (capacitance and conductance) of ultrathin MIS tunnel junctions and non-abrupt MS junctions under modulated bias, $V + V_{AC}\exp(j\omega t)$, have been derived by Gomila [35,36] using coupled kinetic equations which define the occupancy of interface states as a function of applied dc bias, V, bias modulation frequency, ω, and temperature, T. In contrast with previous models, exchange of carriers between interface states and either the metal or the semiconductor has been considered. However, to our best knowledge, no systematic validation of Gomila's model has been performed with experimental data for tunnel MIS diodes.

In this work, the behavior of admittance $Y(V, T, \omega)$ and dc current density $J(V, T)$ characteristics in ultrathin MIS tunnel junctions is illustrated by $Hg//C_{12}H_{25}$—n Si junctions incorporating n-alkyl molecular layers ($d_T = 1.45$ nm) covalently bonded to n-type Si(1 1 1). In order to obtain a reliable density of states distribution from admittance measurements in nonequilibrium MIS devices, this work emphasizes the combined role of dc current density and interface states density, as predicted by the tunnel barrier model. The strong rectification in $J(V, T)$ due to the n-type doping provides a very large range of dc current which is helpful to identify several transport regimes.

The organization of the manuscript is as follows. Section 2 recalls the physics of the tunnel barrier model leading to the admittance $Y(V, T, \omega)$ of ultrathin MIS tunnel junctions. The combined role of dc current density $J(V, T)$ and interface states density distribution $D_S(E)$ in the measured admittance characteristics, in particular the *low frequency capacitance* and *high frequency conductance*, is emphasized and the device response time is introduced. Section 3 describes the experimental methods, including photochemical grafting of alkene molecules on Si(1 1 1), X-ray photoelectron spectroscopy (XPS) characterization of molecular coverage, spectroscopic ellipsometry (SE), dc and ac electrical transport at variable T. Besides $J(V, T)$ measurements in the T range 243–293 K, the admittance $Y(V, T, \omega)$ is characterized in a wide frequency range (10^{-2}–10^7 Hz) in order to investigate the dynamic characteristics of the tunnel barrier, the space charge region and the interface trap distribution. Section 4 is devoted to the admittance spectroscopy characteristics, used to obtain the flat band voltage, V_{FB}, the device response time, τ_R, and the density of interface electronic states, $D_S(E)$. The comparison of the density of states distributions derived from the device response time and from the classical low–high frequency capacitance method (valid for thick MIS devices), respectively, allows to define a "low current density regime" and a "high current density regime". The potential influence of high local current density, e.g. due to some lateral inhomogeneity of the barrier height, on the measured admittance $Y(V, T, \omega)$ is also discussed.

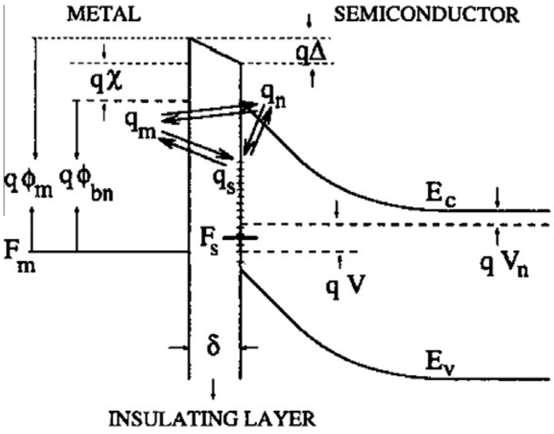

Fig. 1. Energy band diagram and carrier exchange mechanisms at the tunnel MIS interface [36] (reprinted with permission from IOP).

Our experimental results are compared with some predictions of admittance modeling for ultrathin MIS tunnel junctions, in particular the dependence of the low frequency capacitance $C(\omega \approx 0)$ on $J(V, T)$ and the frequency dependence of the electrical modulus. Some model parameters such as the microscopic response time of interface defects and their distribution in energy, $D_S(E)$, are derived from experimental data. While all of the experimental results presented in this work were obtained using $Hg//C_{12}H_{25}$—n Si(1 1 1) molecular junctions, the method is more general and could be applied to any tunnel MIS device.

2. Non-stationary transport model

The non-stationary transport properties (capacitance and conductance) of nonintimate Schottky contacts and MIS tunnel diodes have been derived using coupled kinetic equations which define the occupancy of interface states as a function of applied dc bias, bias modulation frequency and temperature [35,36]. We briefly recall the main hypothesis and the device admittance expression to emphasize the combined role of dc current density $J(V, T)$ and interface states density distribution $D_S(E_C - E_T)$ in the *low frequency capacitance* and *high frequency conductance* and to introduce the device response time directly evidenced in $M''(\omega)$ plots of the electrical modulus.

2.1. Kinetic mechanisms

In the energy band diagram of the MIS tunnel diode with insulator thickness d_T (noted as δ in Fig. 1), the barrier height, ϕ_{BN}, is defined by the metal work function, ϕ_m, and the SC electron affinity, χ. The dc thermionic emission current across the interface is governed by this barrier height and by an attenuation factor $\exp(-\beta^{\circ} d_T)$ due to the tunnel barrier transparency; the parameter β^0 can be derived from the temperature dependence of the apparent barrier height in the thermionic emission regime [15].

Fig. 1 shows that three elementary kinetic processes can be identified:

$$q_n \leftrightarrow q_m; \quad q_s \leftrightarrow q_m; \quad q_s \leftrightarrow q_n \tag{1}$$

in which q_n, q_m, q_s stand respectively for the electrons in the semiconductor, in the metal and at the interface states. If the series resistance (R_S) can be neglected (not true at high J), the applied bias V is the difference $F_m - F_n$ between the metal Fermi level, F_m, and the semiconductor Fermi level, F_n.

In contrast with Gomila's approach, where no restriction on the carrier exchange between interface states and either the metal or the semiconductor has been assumed, previous models of thin MIS junctions restricted the exchange of electrical carriers of interface traps to the SC conduction band [25,29,37,38]. Although resulting expressions of the admittance are quite similar to Eq. (12), the microscopic response times of localized interface states are quite different: a capture–emission time constant is derived from Shockley–Read–Hall parameters [22] in the former models