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Direct measurement of majority-carrier quasi-Fermi levels in Schottky barrier and metal-insulator-semiconductor diodes

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A novel point contact technique for directly measuring Fermi-level variations in biased semiconductor diodes is described. This technique is applied to Al/*n*-Si and Al/SiO_2/*p*-Si structures, and the results are shown to be in good agreement with the drift/diffusion limit of diode transport theory.

The issue of properly defining and calculating the local electrochemical potential for electrons under nonequilibrium conditions plays a crucial role in determining the transport properties of Schottky barriers (SB) and metal-insulator-semiconductor (MIS) structures. This is particularly true in the latter case when the insulator thickness is small enough to permit substantial tunneling currents. In this communication we will demonstrate a new experimental technique for directly measuring nonequilibrium electrochemical potentials (quasi-Fermi levels). Results will be shown for Schottky and MIS diodes and compared directly to Fermi-level profiles calculated theoretically. In addition, we will discuss some of the experimental difficulties involved in this method and the manner in which the sample preparation method and the presence of the measuring probe itself perturb the quantities that we are trying to determine.

A convenient vehicle for discussing carrier transport in Schottky barriers is the combined thermionic emission/diffusion theory of Crowell and Sze (CS).[1] This theory directly exhibits the two extreme limits of this transport problem. CS start by assuming that a local value of the (quasi) Fermi level, E_F, can be defined essentially everywhere in the depletion region of a biased Schottky barrier. If the electric fields are not too high (limiting expressions have been derived by Stratton[2] and others[3]), the local majority-carrier density (in the *n*-type case) and current flux can be written as

$$n(x) = N_c \exp\{-[E_c(x) - E_F(x)]/kT\} \tag{1}$$

and

$$J(x) = n(x)\mu \frac{\partial E_F(x)}{\partial x}, \tag{2}$$

where $E_c(x)$ and μ have their usual meanings, and N_c is the effective conduction-band density of states.

The actual current passing over the top of the barrier is defined separately as

$$J(0) = ev_r[n(0) - n_0], \tag{3}$$

where n_0 is the equilibrium ($V = 0$) carrier density in the semiconductor at $x = 0$ and v_r is a "recombination velocity" calculated to be $\frac{1}{4}$ of the carrier thermal velocity[4] v_{th}. The position of E_F at $x = 0$ is now regarded as an adjustable quantity determined by equating Eqs. (2) and (3). In the "thermionic limit" of this theory $E_F(x)$ is essentially flat throughout the depletion region. This statement is true provided the quasi-Fermi level does not approach either band too closely (weak forward or reverse bias). In this limit the transport of carriers through the structure is limited by the difficulty of carrier emission at the metal/semiconductor interface and not by the drift and diffusion process in the depletion region. In the opposite limit when

$$\mu E(x = 0) \ll v_{th}/4, \tag{4}$$

there is essentially no discontinuity of $E_F(x)$ at $x = 0$. This is the drift/diffusion limit of this formalism.

Since $E(x = 0) \propto N_d^{1/2}$ the drift and diffusion limit applies at lower doping densities. For silicon, Eq. (4) is well satisfied at the doping densities and electric fields employed in the measurements discussed here. Thus, the CS theory predicts an easily calculable variation of $E_F(x)$ for our Schottky barrier samples; this variation can be deduced by numeric integration of Eq. (2) given Eq. (1) and a parabolic variation (constant doping density) of $E_c(x)$.[4]

In the case of MIS structures, there is a further impediment to carrier emission at $x = 0$ because of the necessity for charge carriers to tunnel through the insulator. In the case of metal/SiO_2/Si structures where the insulator thickness is greater than ~ 100 Å, diode currents become vanishingly small and $E_F(x)$ is flat throughout the semiconductor depletion region; this superficially resembles the thermionic limit for Schottky barriers. As the insulator thickness is reduced from, say, 100–20 Å, the discontinuity in $E_F(x)$ at the interface will become vanishingly small at a point which not only depends on oxide thickness, but on the precise details of the tunneling process, such as the Si/SiO_2 interface state density and the number of resonant tunneling centers in the oxide. Experimental studies in this area have yet to provide a detailed understanding of this problem in the Si/SiO_2/metal system. Recent work has emphasized that thin layers of furnace grown SiO_2 are generally not homogeneous in thickness[6–8] leading to MIS diodes whose transport properties can be quite inhomogeneous and process dependent.[9] It is expected that the recent emphasis on improved thin oxides processed with appropriate post-oxidation anneals or grown at temperatures above the oxide flow point with rapid thermal oxidation[10] (RTO) techniques will promote a better understanding of this problem.

To determine $E_F(x)$ we propose that a small area (< 100 Å diameter) metal/semiconductor contact be made

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on a surface which is parallel to the direction of current flow through the Schottky barrier or MIS diode. In practice, the probe contact can be achieved with a small radius ($\sim$ 1000 Å) tungsten needle and the surface is prepared by cleaving the diode along a plane parallel to the bulk current flow. Since the object of the measurement is to measure the $E_F(x)$ profile characteristic of the unperturbed, bulk current flow, it is necessary for us to address the way in which the measurement process, itself, unavoidably perturbs this flow. For instance, surface charge will bend the semiconductor bands at the cleaved surface, causing some deviation of the current flow as charge carriers avoid the surface depletion region. In addition, charge rearrangement caused by the probe contact itself will alter the near-surface diode current. We will discuss the importance of these effects after presenting our experimental data.

The measurements were made with an apparatus having some similarities to the scanning tunneling microscope (STM).[11] While it lacks some of the sophisticated vibration filters which allow typical STMs to maintain 1–50-Å probe tip/sample distances with <0.1-Å precision, it incorporates other features which make it useful for a wide variety of measurements. A finely sharpened tungsten needle (500–1500-Å tip radius) is controlled by three orthogonally coupled single-axis mechanical stages containing 10-μm range piezo stacks for precision (<100 Å) tip positioning. Mechanical springs are used to preload the stage ways. Piezo drive voltages are provided by power supplies under control of an HP86 minicomputer. The entire probe positioning system is located on the stage of a Hitachi S-570 scanning electron microscope (SEM). The sample is mounted on the standard Hitachi stage and is separately positionable under the electron optics. The usual mode of measurement is for the probe axis to be $\sim 45°$ from the incident electron beam and the surface normal, allowing probe positioning under full SEM backscattered electron imaging. While some positional uncertainty is caused by "skating" along the surface with this choice of probe incidence angles, we have found that lowering the probe tip with its axis normal to the Si almost always deforms the tip profile after repeated contacts. A Keithley 619 electrometer[12] is used in the voltage mode (input impedance $> 10^{14}\ \Omega$) for both probe lowering and contact potential measurements, again under control of the HP86 minicomputer. It is worth reminding the reader that the quantity measured during a contact measurement of this type is the electrochemical (not electrostatic) potential difference between the sample area just below the probe tip and the reference electrode (the diode back contact, in this case). Because of the high impedance typical of probe tip/silicon contacts, 20–60-s measurement times were typically required to fully charge the cable/electrometer input stage.

Samples selected for this study were of two types. The Schottky barrier samples were fabricated by Al evaporation on lightly phosphorus-doped ($\sim 5\times 10^{15}\ \mathrm{cm}^{-3}$) ⟨100⟩ epitaxial layers grown on heavily doped silicon substrates. Metal/insulator/semiconductor barrier structures were made on ⟨100⟩ 2Ω cm boron-doped wafers which had a thin (~ 33 Å) layer of SiO_2 grown by a low-temperature (600 °C) thermal anneal in dry oxygen. Ohmic back contacts were sintered aluminum, while the front metallization was a 2-μm-thick evaporated/electroplated layer of the same metal. Doping profiles were obtained on each sample from Mott–Schottky plots of the 1-MHz diode capacitance versus bias.

The probe scans were made on smooth surfaces approximately normal to the wafer plane obtained by a back surface scribe and break procedure. Because the ⟨111⟩ planes are the preferred cleavage planes in silicon, numerous samples had to be broken to produce the occasional ⟨100⟩ surface orientation suitable for these measurements. No cleaning steps of any sort were carried out on the broken edge, and introduction of the specimen into SEM vacuum conditions (10^{-6}–10^{-7} Torr) was accomplished within a few minutes after the scribe and break procedure. A schematic view of the measurement geometry is shown in Fig. 1.

While we had the capability to position the probe tip near the front metallization in the SEM imaging mode, we were forced to forego the use of this positioning aid for our measurements because even momentary electron beam exposure of our sample surface caused large alterations of the near surface potential profiles which took from hours to days to disappear. Apparently, beam-induced carbonization of surface hydrocarbon contaminants is responsible for this behavior; this phenomenon forced us to locate the front surface metallization with a "blind" walk-and-measure procedure. Of course, post-measurement SEM analysis could be made to verify the probe location. Many measurements (10–30) were made on several specimens to check the reproducibility

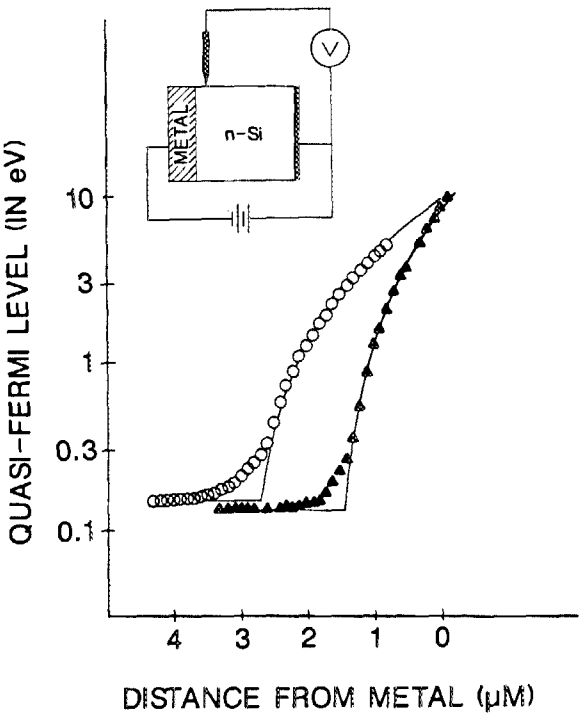

FIG. 1. Quasi-Fermi level vs needle position for two different Al/SiO_2/p-Si diodes (reverse) biased at $+10$ V vs the tungsten point probe position. About ~ 0.15 V are dropped across the back contact and bulk of the semiconductor. Solid lines are the drift/diffusion profiles of $E_F(x)$ calculated from Eq. (5) using the doping densities determined from 1-MHz capacitance data on each sample. The inset shows a schematic view of the measurement technique on a Schottky diode.

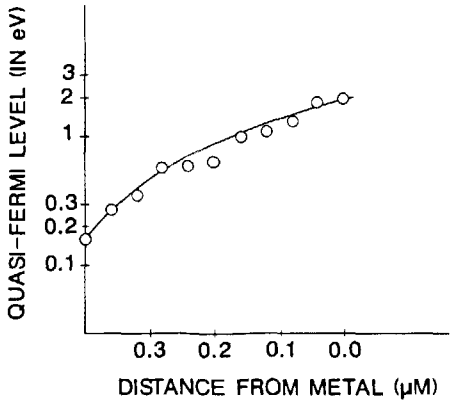

FIG. 2. Measured quasi-Fermi level profiles for a Al/n-Si Schottky barrier diode (reverse) biased at -2 V. Solid lines are the drift diffusion variation of $E_F(x)$ calculated from Eq. (5) and 1-MHz C-V data.

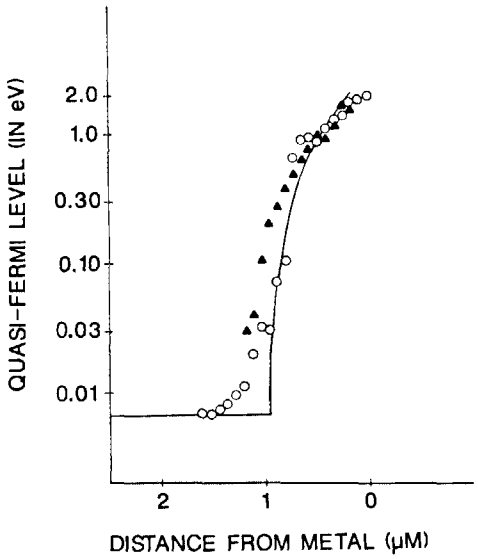

FIG. 3. Quasi-Fermi level profiles for two separate experimental runs (different positions along the MIS interface) made on a Al/SiO_2/p-Si diode biased at $+2$ V. Solid lines are from Eq. (5) and 1-MHz C-V data.

of the data and to compensate for the occasional thermal drift (typically tenths of a micrometer per hour) of the probe position. Typical data were noisier than that shown here. Only occasionally ($\sim 10\%$–20% of the time) could we obtain data as good as those shown in Figs. 1–3. We believe that variable tip/sample surface cleanliness causes these problems. Some attempts to sputter clean or metal coat the tungsten probe tips produced no consistent improvement in data reproducibility.

Some time was spent examining the Schottky barrier (SB) and MIS samples at large reverse biases to confirm that the dimensions of the rather wide depletion regions produced this way conformed to theoretical expectations. Data for two MIS diodes are shown in Fig. 1. SB samples yielded similar curves. On this scale small (0.1–0.3 eV) drops in $E_F(x)$ at the Si/SiO_2 interface are not resolvable, and we are just probing the detailed shape of the depletion regions. The numerically integrated solution for $E_F(x)$ from the drift and diffusion equations (the appropriate limit of the CS theory at these doping levels) is

$$E_F(x) = kT \ln\left(1 + e^{eV/kT} \frac{\int_w^x e^{E_c(x')/kT} dx'}{\int_w^0 e^{E_c(x')/kT} dx'}\right), \qquad (5)$$

where e is the electronic charge and $E_c(x)$ is the appropriate (majority carrier) band edge measured from the bulk Fermi-level position. For constant doping density $E_c(x)$ is given by

$$E_c(x) = (\phi_B + eV)[(x/w) - 1]^2 + \zeta_0, \qquad (6)$$

where w is the depletion width, ζ_0, the energy separation between the bulk Fermi level and the majority-carrier band, and ϕ_B is the barrier height[4] at $x = 0$. Plots of Eq. (5) are shown in Fig. 1 as solid lines. The finite asymptote is the combined potential drop across the back contact (held at $V = 0$) and the silicon bulk. Except for a region $\sim 1\,\mu$m wide near the depletion edge, there is good agreement between theory and experiment. We believe that the deviations seen near $x = w$ reflect the influence of the depletion region surrounding the tungsten/silicon contact point. This tends to "smear out" the sharp onset in $E_F(x)$ expected theoretically. Once the needle tip has entered the Al/Si depletion region by $\sim 0.5\,\mu$m, it is reasonable to expect that its presence will not substantially alter the near surface value of $J(x)$ [and hence $E_F(x)$].

Figures 2 and 3 show SB and MIS diode data taken at lower reverse biases, where the issues of the precise x dependence of E_F and any discontinuity at $x = 0$ can be examined more closely. For the SB case (Fig. 2) there appears to be reasonably good agreement between theory and experiment, although the scatter precludes us from claiming that the discontinuity in E_F at $x = 0$ is less than ~ 0.2 eV. The data are certainly consistent with the drift and diffusion limit prediction of CS.

In the MIS case, the data show roughly the same scatter as in Fig. 2 which prevent us from precisely determining the interface discontinuity in $E_F(x)$. The same "smearing effect" is clearly seen near $x = w$ and the overall agreement with the drift and diffusion calculation is fairly good. The tendency of the data to show a slightly broader depletion region than the capacitatively determined value at these lower reverse biases may be due to the effects of surface states at the cleaved surface or perhaps to doping nonuniformities. Band bending at this surface will force the current lines to be nonparallel which should "stretch out" the measured $E_F(x)$ profile. This effect should become negligible at larger depletion widths (Fig. 1). Again, the scatter in the data forces us to be somewhat tentative in our explanation of these effects.

We have shown that the measuring technique proposed to determine $E_F(x)$ yields reasonable results for quasi-Fermi level profiles which are in agreement with the basic predictions of prior SB transport calculations. In the case of the Al/SiO_2/p-Si system, data scatter prevents us from making a precise determination of the interface discontinuity in $E_F(x)$. Prior measurements[9] of the equilibrium properties of these diodes have indicated rather large (~ 0.7 eV) values for ϕ_B which alter slightly the band bending profile near

$x = 0$ due to inversion charge. These changes in $E_v(x)$ have not been incorporated in the theoretical curves of Figs. 1 and 3 because they are small compared to the data scatter. These inversion effects will, however, tend to limit the buildup of any large $E_F(x = 0)$ discontinuity at reverse biases, and so in some sense this system is not an ideal one for observing these effects given the scatter seen here.

What are the prospects for improving the measurement precision? Because of the "skating" of the tungsten point as it first contacts the surface and the necessity for some applied probe pressure (to break through the native oxide perhaps?), we believe that the uncertainty of the data in Figs. 1–3 is largely in the distance coordinate. While we cannot directly observe the tungsten point with the SEM beam on during the actual acquisition of "good" data, we have seen this "skating" phenomenon during probe lowering and touching routines on a "postmortem" basis. This suggests that measurements on diodes made in material doped in the 10^{13}–10^{14} cm^{-3} range will have a factor of 3–10 better precision because of the expanded range of variation of $E_F(x)$. These are planned for the future.

We conclude that this measurement technique provides a novel, direct measurement of depletion region properties. Evidence is found for the applicability of the Crowell and Sze[1] Schottky barrier transport theory, and some effects are seen of the influence of the probe/semiconductor barrier itself on the measured data. No strong evidence is seen for the effect of surface states, and in particular we think these effects should be small for data taken near the semiconductor/metal interface.

In addition to its possible utility in settling issues of transport in these MIS structures, this technique provides a unique method for investigating microscopic doping and/or barrier height inhomogeneities in SB and MIS diodes.

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[1]C. R. Crowell and S. M. Sze, Solid-State Electron. **9**, 1035 (1966).
[2]R. Stratton, Phys. Rev. **126**, 2002 (1962).
[3]E. J. Ryder and W. Shockley, Phys. Rev. **81**, 139 (1951).
[4]For low doping densities it is permissible to neglect the effect of image force corrections to $E_c(x)$.
[5]Some of these effects are discussed by E. H. Rhoderick, in *Metal-Semiconductor Contacts* (Clarendon, Oxford, 1980), p. 121.
[6]T. Hattori and T. Nishina, in *The Physics of SiO_2 and Its Interfaces*, edited by S. T. Pantelides (Pergamon, New York, 1978), p. 379.
[7]A. H. Carim and A. Bhattacharyya, Appl. Phys. Lett. **46**, 872 (1985)
[8]A. H. Carim and R. Sinclair, J. Electrochem. Soc. **134**, 741 (1987)
[9]M. A. Butler and C. H. Seager, J. Appl. Phys. **60**, 2137 (1986).
[10]J. Nulman, J. P. Krusius, and A. Gat, IEEE Electron Device Lett. **EDC-6**, 205 (1985).
[11]G. Binnig, H. Rohrer, C. H. Gerber, and E. Weibel, Phys. Rev. Lett. **49**, 57 (1982).
[12]Keithley Instruments, 28775 Aurora Rd., Cleveland, OH 44139.

Effect of carbon concentration on the electrical properties of liquid-encapsulated Czochralski semi-insulating GaAs

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Effects of carbon concentration on the electrical properties of liquid-encapsulated Czochralski semi-insulating GaAs crystals are investigated quantitatively for the first time by keeping other parameters such as melt stoichiometry, EL2 concentration, and dislocation density almost the same. Its dependence can be well explained by the mixed conduction model.

Semi-insulating (SI) GaAs crystals grown by the liquid-encapsulated Czochralski (LEC) method[1] have been considered to be promising materials for fabricating high-performance integrated-circuit devices. LEC GaAs shows a semi-insulating property, even in undoped crystal. It is commonly accepted that this property is due to the compensation of shallow acceptor carbon by midgap donor EL2.[2] To ensure high and uniform activation of implanted Si, the concentration of the residual carbon is required to be as low as possible.[3] Thus, EL2 and carbon play an essential role in determining the electrical properties of SI GaAs.[2,4] However, there are few quantitative analyses of the effect of carbon concentration on the electrical properties of LEC SI GaAs crystals.

In this paper, we investigate the electrical properties of LEC SI GaAs crystals whose carbon concentrations are controlled in wide range and analyze them quantitatively by the

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