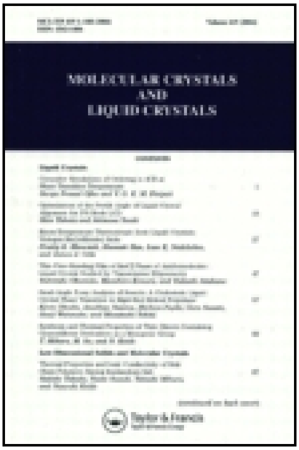

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Frequency-Dependent Admittance of Schottky Barriers at the Aluminium/Poly (3-Methylthiophene) Interface

Henrique L. Gomes [a] & D. Martin Taylor [a]
[a] Institute of Molecular and Blomolecular Electronics, University of Wales, Dean Street, Bangor, Gwynedd, LL57 1UT, UK
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FREQUENCY-DEPENDENT ADMITTANCE OF SCHOTTKY BARRIERS AT THE ALUMINIUM/POLY(3-METHYLTHIOPHENE) INTERFACE

HENRIQUE L. GOMES AND D.MARTIN TAYLOR
Institute of Molecular and Biomolecular Electronics, University of Wales, Dean Street, Bangor, Gwynedd LL57 1UT, UK.

Abstract AC admittance measurements have been made from 10 Hz to 1 MHz so as to establish the conditions under which reasonable estimates of dopant density and diffusion potential may be made from C-V measurements. Cole-Cole plots are shown to provide a means of characterising devices in terms of the spread in their relaxation times. The effects of thermal annealing on device parameters are described.

INTRODUCTION

Measuring the admittance of semiconductor materials and devices over a wide frequency range has proved particularly useful in developing an understanding of their behaviour. Although detailed measurements of this type were made on Schottky barriers formed from polyacetylene[1] few such studies have been made on other polymers, most authors simply carrying out capacitance-voltage measurements at one frequency only. Here we report results obtained from an in-depth study of the dc and ac properties of Al/poly(3-methyl thiophene) (PMeT) Schottky barriers.

EXPERIMENTAL

Films of PMeT were grown electrochemically on evaporated gold electrodes in a conventional 3-electrode cell. The electrolytic medium, composed of propylene carbonate, 0.1 M tetrabutylammonium tetrafluoroborate (dried before use) and 0.5 M 3-methylthiophene was degassed by nitrogen bubbling for 20 min. Electropolymerisation was carried out in two stages[2] by applying a constant potential (2.0 V vs Ag) for 5 s to ensure a high density of nucleation centres[3] on the gold surface after which the polymer was grown galvanostatically at 0.4 mA/cm^2. Films were electrochemically undoped for 45 min at either 0.0 or 0.1 V (vs Ag) to control residual dopant density, then rinsed with acetone and heated to $50^{\circ}C$ in

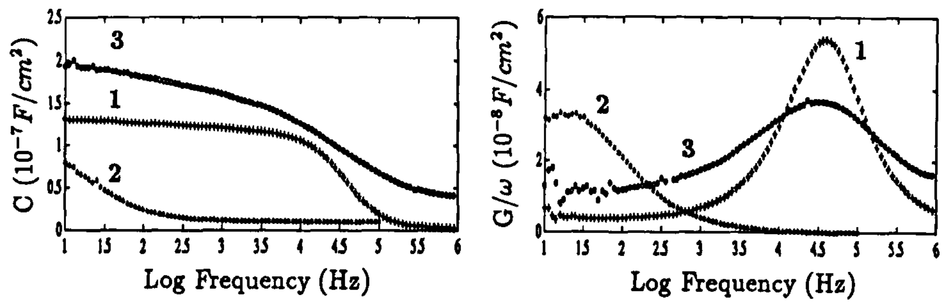

FIGURE 1 Frequency dependence of C and G/ω for diodes 1,2 and 3.

TABLE I Device parameters deduced from measurements.

Device	d (μm)	V_{RED} (V vs Ag)	$\alpha^{‡}$	V_d (V)	N^* (m^{-3})
1	1.2	0.0	0	1.3	2.0×10^{17}
2	0.5	0.0	0.23	-	-
3	0.2	0.1	0.44	1.0	4.7×10^{17}
$3^{†}$	0.2	0.1	0.44	0.9	1.8×10^{17}

† After final anneal under vacuum to 90°C.
‡ After correcting for the dc conductance of the device.
* Assuming $\varepsilon_s = 6$.

vacuum prior to deposition of aluminium electrodes by evaporation to form the rectifying contact. The admittance measurements were carried out under vacuum using an Impedance Analyzer.

RESULTS AND DISCUSSION

Figure 1 shows the frequency-dependence of C and G/ω for the diodes listed in Table I. All devices show a major dispersion consistent with the simple equivalent circuit in Figure 2(a) (inset), the central frequency of which lies between 10 Hz and 50 KHz. The components R_d, C_d and R_b, C_b are respectively the resistances and capacitances of the depletion and bulk regions of the device. It is readily shown that if $R_d \gg R_b$ the relaxation time, τ, of the circuit is given by

$$\tau = R_b(C_d + C_b). \quad (1)$$

We see, therefore, that the relaxation frequencies in Figure 1 should be determined by (i) film thickness and (ii) doping density, N_A, since

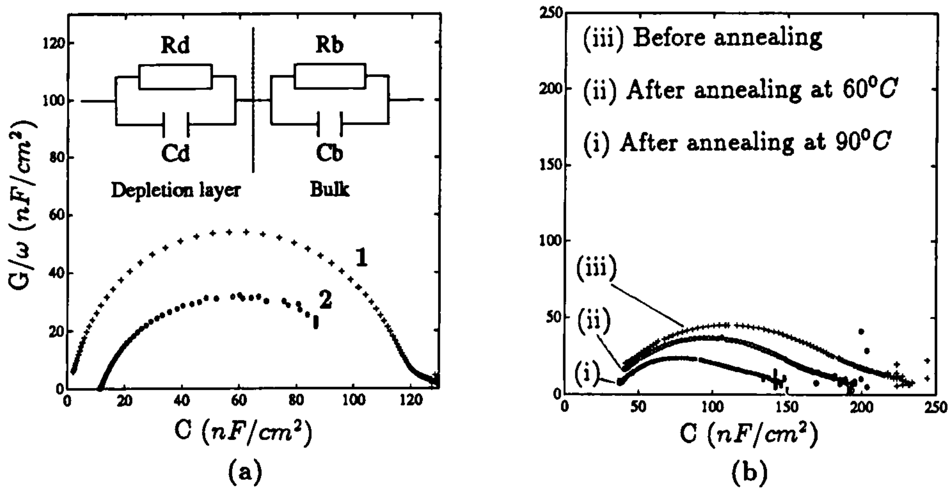

FIGURE 2 Cole-Cole plots for (a) devices 1 and 2 and (b) device 3 (i) before and (ii) after thermal anneal.

R_b is inversely proportional to N_A and C_d ($\gg C_b$) proportional to $N_A^{1/2}$. Apparently, N_A is smaller in device 2 (undoped at 0.0 V vs Ag) than in devices 1 and 3 (undoped at 0.0 and 0.1 V respectively). In the thicker device 1, the undoping process appears to have been less efficient.

Admittance data for dielectric materials is often presented in a Cole-Cole[4] plot which is described by the equation

$$(\varepsilon^* - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty) = 1/\{1 + (j\omega\tau)^{1-\alpha}\} \qquad (2)$$

where ε^* is the complex relative permittivity at angular frequency ω, ε_s and ε_∞ the static and high frequency relative permittivities respectively, τ a relaxation time and α a parameter characterising the relaxation time distribution. For a Debye response, $\alpha = 0$, the relaxation time is single-valued and the Cole-Cole plot is a semicircle. When $0 < \alpha < 1$, the plot becomes an arc, with its centre below the abscissa. Clearly, device 1 shows classic Debye behaviour with α close to zero.

Curve (iii) in Figure 2(b) shows that device 3 departs significantly from simple Debye behaviour with the data being fitted best when $\alpha = 0.44$, indicating a large spread in relaxation times. Device 3 as well as being the least undoped is also the thinnest, so the increase in α with decreasing film thickness suggests that the spread in relaxation times may arise from a statistical variation in film thickness.

Capacitance-voltage Characteristics

The relationship between device capacitance and applied voltage for a Schottky barrier diode is given by

$$1/C^2 = 2(V_d-V)/q\varepsilon_s\varepsilon_o N_A \qquad (3)$$

where q is the electronic charge, ε_o the permittivity of free space and V_d the diffusion potential. A plot of $1/C^2$ vs. V should then yield values for N_A and V_d. From Figure 3(a) it is clear that care is required in choosing the frequency at which to perform a C-V measurement. At low

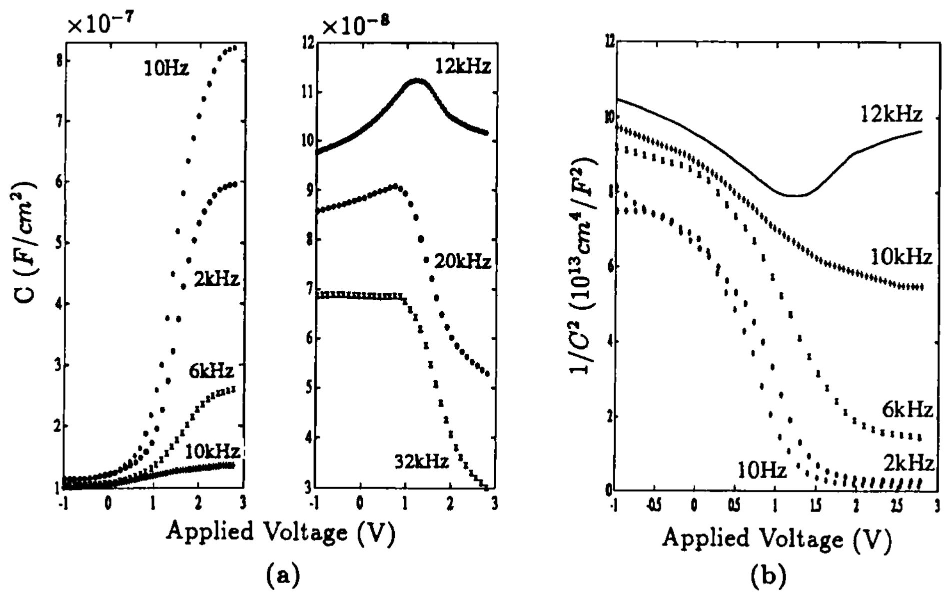

FIGURE 3 (a) C-V and (b) $1/C^2$ vs V curves at various frequencies for device 1.

frequency, R_b effectively short-circuits C_b so the measured capacitance equals C_d. Applying more positive voltages to the gold electrode decreases the depletion region width thereby increasing C_d. At higher frequencies, the decreasing reactance of C_b increasingly influences the measurement so that C no longer equals C_d. Comparing Figures 1 and 3(a) we deduce that to minimise this effect in C-V measurements it is necessary to operate at a frequency which is at least an order of magnitude below that of the main dispersion. For device 1 this condition is readily achieved but not for device 2 which would require measurements at or below 1 Hz. For device 3, the presence of a broad underlying dispersion makes it difficult to identify a suitable low frequency at which to measure C_d accurately.

$1/C^2$ vs V curves for device 1 (Figure 3(b)) at 10 Hz and 2 KHz, although coinciding over most of the range show significant curvature between -1 V and +0.5 V. However, by extrapolating the moderately linear region between 0.5 and 1.0 V the estimates of V_d and N_A given in Table 1 were made. Obviously from the plots obtained above 2 KHz, both N_A and V_d will be seriously overestimated. The values deduced for device 3 at 100 Hz (Figure 4(a)) are also given in the table but may be in error because of the broad underlying dispersion seen in Figure 1.

Effect of Thermal Annealing

Device 3 was taken through several stages of thermal annealing under vacuum in which the temperature was cycled to progressively higher values. The maximum temperature attained was 90°C. The effect of annealing is marked (see Figures 2(b) and 4(a)). We also show for completeness in Figure 4(b) the improved diode behaviour following annealing; the rectification ratio at 1 V increases from 330 to 5900 and at 2.5 V from 2×10^4 to 5×10^4. From the I-V plot it is seen that annealing

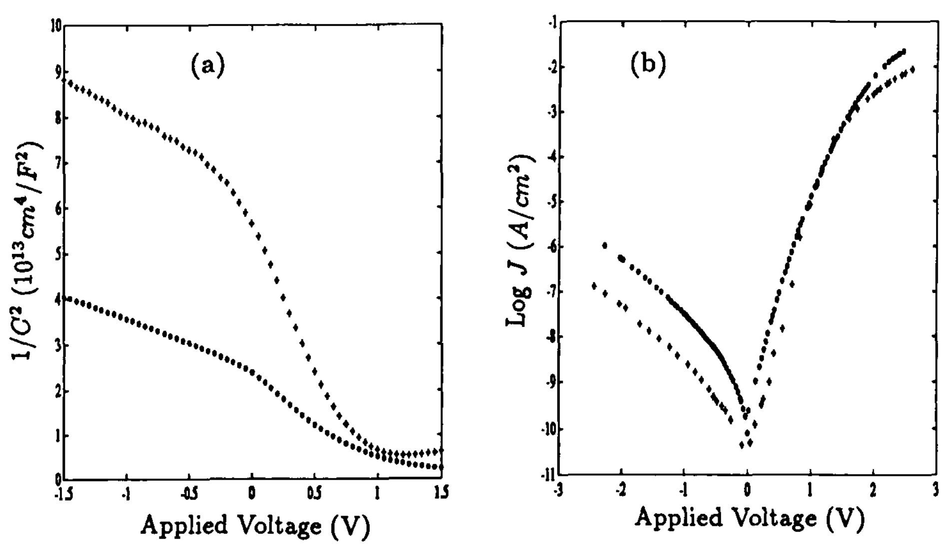

FIGURE 4 (a) $1/C^2$ vs V at 100 Hz and (b) J-V plots for device 3 (o) before and (+) after thermal anneal.

has reduced device current both in reverse and in high forward bias, suggesting that doping density has been decreased. This appears to be confirmed by the bigger slope in curve 2 of Figure 4(a). Interestingly, the value deduced for α in Figure 2(b) remains unchanged implying that while the total number of relaxing entities has been reduced, the distribution in their relaxation times remains unchanged.

CONCLUSIONS

It has been shown that unless the admittance of Schottky barrier diodes is mesured over a wide frequency range then estimates of doping density and diffusion potential from C-V plots may be grossly in error because of incorrect choice of measurement frequency. In highly undoped devices this may mean carrying out C-V measurements at subhertz frequencies. In thinner, more highly doped devices, even though the main device relaxation is at high frequencies, the low frequency C-V plot will be complicated by the presence of a significant dispersion which may arise from a variation in film thickness over the device or perhaps from hopping between dopant-related states. This dispersion has a marked effect on the Cole-Cole plot which changes from an almost perfect semicircle to a depressed arc. Thermal annealing of the device showing this behaviour reduces the maximum ac loss associated with this process but has little effect on the relaxation time distribution parameter, α.

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