Properties of metal/polyacetylene Schottky barriers

P. M. Grant, T. Tani,[a] W. D. Gill, M. Krounbi, and T. C. Clarke
IBM Research Laboratory, San Jose, California 95193

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Rectifying barriers of undoped and lightly doped *trans*-$(CH)_x$ films with low work function metals have been investigated. *I-V* and *C-V* measurements were used to explore the junction properties. The junction characteristics were found to be Schottky-like in the large sense accompanied by significant differences in detail. Using *C-V* measurements to determine the carrier concentration, we found the carrier mobility to be concentration dependent.

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Recently the electronic properties of polyacetylene, $(CH)_x$ have undergone intensive investigation due to the discovery that treatment with strong oxidizing or reducing agents leads to a *p*- or *n*-type material with conductivities ranging from insulating all the way up to metallic levels.[1-3] Much research has centered on the two extremes of conductivity, yet one of the most interesting regimes is the physics of the material at semiconducting doping levels. It is in this area that practical applications of many materials occur and the issue is especially pertinent to $(CH)_x$ since theoretical models, at least, suggest that it may be the first organic compound to share several electronic properties in common with inorganic covalent semiconductors.[4] One universal manifestation of semiconductor behavior has been the ability to form Schottky barriers to metals with appropriate work functions. The properties of such junctions with semiconducting *trans*-$(CH)_x$ comprises the subject matter of this paper. Results of Schottky barrier formation to semiconducting Si and GaAs where heavily doped *trans*-$(CH)_x$ was used as the metal contact have been reported,[5] as have results of heterojunctions between semiconducting $(CH)_x$ and II-VI compounds.[6] However, we report here the first results for Schottky diodes in which $(CH)_x$ was the only active semiconductor. We have previously reported the photovoltaic response[7] and ac conductivity[8] of these devices—our main purpose now is to determine the nature of the junction profile and to obtain information on oxidant-induced acceptor levels in both doped and undoped *trans*-$(CH)_x$.

Figure 1 shows the potential distribution within a classic Schottky barrier between a low work function metal and a *p*-type semiconductor and defines the notation used for the junction parameters throughout this paper. Intrinsic *trans*-$(CH)_x$, as well as its oxidant-doped form is *p*-type as the result of the removal of electrons from an otherwise filled valence band consituted from (C2*p*) π-electron overlap by stray impurities and purposefully introduced oxidizing agents. One of the phenomena expected to occur in a Schottky barrier depletion region is the photovoltaic effect which is depicted in Fig. 1 as the excitation and separation of electron-hole pairs under illumination. The threshold of the photovoltaic response can be considered the experimental definition of the conventional single-particle semiconductor band gap. Our measurements alluded to earlier resulted in a value for E_G of 1.48 eV in *trans*-$(CH)_x$.[7] Analysis of the current-voltage (*I-V*) and capacitance-voltage (*C-V*) response functions determine other junction parameters such as the depletion width, acceptor concentration, barrier height, and built-in potential. By combining these data with other transport measurements, one can get order-of-magnitude estimates of the majority-carrier mobility.

Our sample configuration is shown in Fig. 2. Sapphire was used for the substrates, and electrodes M1 and M2 were vacuum deposited by metallic evaporation. The $(CH)_x$ films were synthesized at -77 °C from acetylene gas using a Zeigler-Natta catalyst[9] which had been coated on the substrate surface and layer M1. The films were subsequently heated to form completely *trans*-$(CH)_x$. Usually the electrode M1 metal was chosen to form the blocking contact and a thick layer of gold deposited as M2 to assure adequate contact to the rough outer surface of the film and, at the same time, provide an ohmic contact. Because of its relatively low work function, we used principally indium ($\varphi_{In} = 4.12$ eV) as our blocking contact material. On the other hand, gold has a relatively large work function ($\varphi_{Au} = 5.1$ eV), and it indeed proved to form an ohmic contact to *trans*-$(CH)_x$. The extent of doping was sometimes monitored by measuring the resistivity of another *in situ* $(CH)_x$ film placed beside the junction sample while both

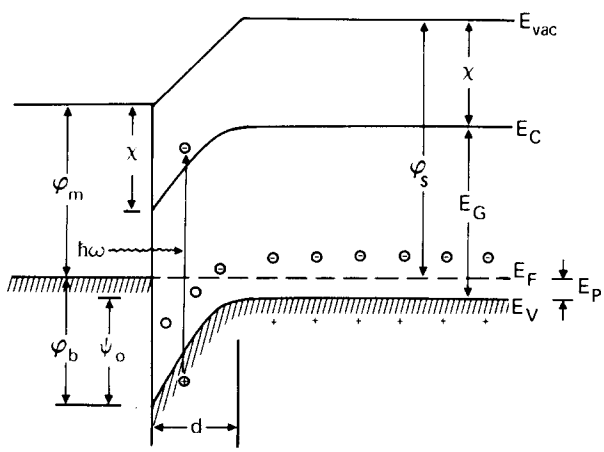

FIG. 1. Junction profile for a low work function metal contact to *p*-type *trnas*-$(CH)_x$ under zero bias with no intervening surface states. This figure defines the symbols used in the text.

[a] IBM Japan World Trade Fellow. Present address: Department of Applied Physics, Faculty of Engineering, University of Tokyo, Tokyo, Japan.

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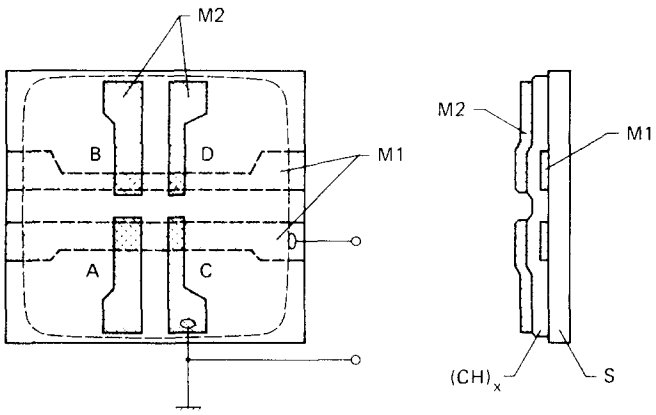

FIG. 2. Sample configurations for the junction transport measurements. S is a sapphire substrate, M1 and M2 are metal electrodes, respectively.

were exposed to the oxidizing agent. In most cases, the resistivity was measured *a posteriori* on the junction sample by predepositing gold as one of the M1 contacts. Film thicknesses were determined using reflectance interferometric techniques. When aluminum ($\varphi_{Al} = 4.28$ eV) was used to make the rectifying contact, it was deposited in position M2 to avoid aluminum oxide formation problems that would have arisen in position M1. Practically all sample handling and measurements were performed in a dry box or *in vacuo* with exposure to air kept within 1 or 2 min. On any given sample, each junction yielded nearly identical characteristics. For the *I-V* characteristic measurements, a Keithley 225 current source was used and the voltage drop detected with a high input impedance Keithley 602 electrometer or a Keithley 171 multimeter. The *C-V* characteristics were measured with a variety of instrumentation: a Boonton 75 C bridge, a General Radio 1615-A bridge, a HP 4261-A *LCR* meter, and a specially designed, locally built Schering bridge for low frequencies. In all our capacitance measurements, the sample was assumed to constitute a parallel *RC* equivalent circuit.

We now discuss the static *I-V* characteristics taken at room temperature. Figures 3–5 summarize our results. Figure 3 shows the behavior of an In/$(CH)_x$ junction undoped

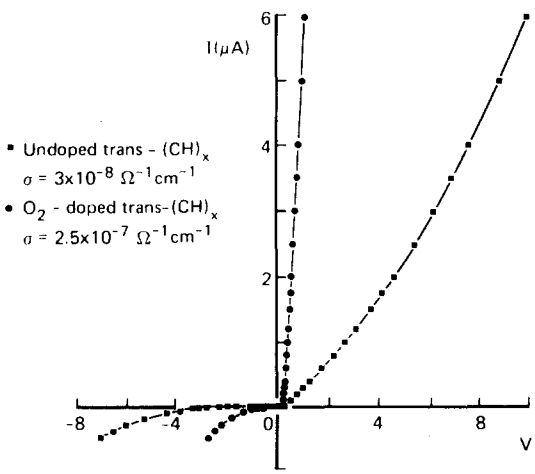

FIG. 3. *I-V* characteristics of undoped and lightly O_2-doped In/*trans*-$(CH)_x$ barriers.

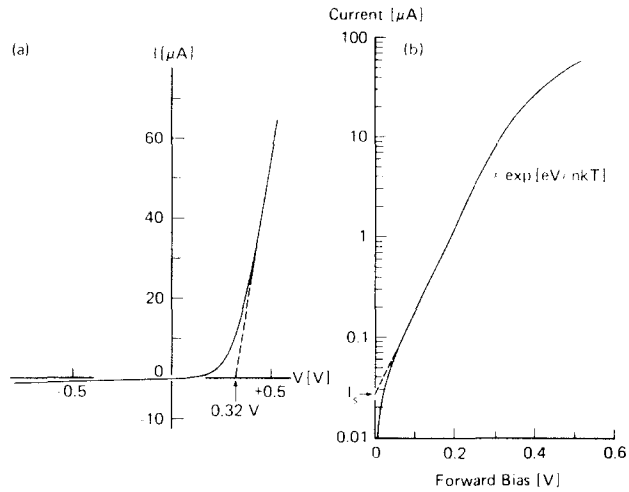

FIG. 4. (a) *I-V* characteristics of a lightly AsF_5-doped In/*trans*-$(CH)_x$ barrier. (b) log I vs V of the same data in the forward bias region.

and after doping with O_2. The respective conductivities were 3×10^{-8} and $2.5\times10^{-7}\ \Omega^{-1}\ cm^{-1}$, and the back-to-forward ratios approximately 75 and 100. In Fig. 4, data are shown for a sample more heavily doped with AsF_5, whose conductivity was $8.4\times10^{-3}\ \Omega^{-1}\ cm^{-1}$ and back-to-forward ratio 140. For purposes of comparison, the back-to-forward resistance ratio of an Au/*n*-Si Schottky diode is typically 10^{10}. A compilation of all junction resistances is given in Table I. The semilog plot of Fig. 4(b) shows the AsF_5-doped device forward characteristic to behave nearly exponentially on bias voltage. From the slope of the linear portion of the plot, we obtain for the diode ideality parameter $n = 1.98$ [$n \equiv (e/kT)\partial V/\partial \ln J$]. At a foward bias poten-

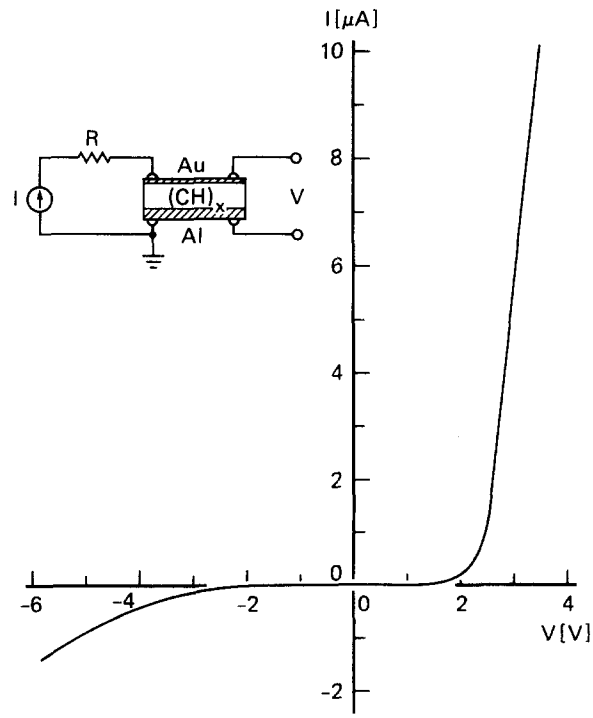

FIG. 5. *I-V* characteristics of an undoped Al/*trans*-$(CH)_x$ barrier. Note the similarity to the undoped sample of Fig. 3.

TABLE I. Diode resistances in the forward (f) and back (b) bias directions for *trans*-$(CH)_x$ junctions.

Sample	R_f(kΩ)	R_b(MΩ)	R_b/R_f
Undoped	1000	74	74
O_2	160	19	118
AsF_5	3	0.425	142

TABLE II. Summary of material parameters derived from junction properties of In/*trans*-$(CH)_x$ Schottky diodes as a function of doping level.

Sample	$\sigma(\Omega^{-1}\text{cm}^{-1})$	$N_A(\text{cm}^{-3})$	d(Å)	$\mu(\text{cm}^2/\text{V sec})$
Undoped	3×10^{-8}	6×10^{16}	740	3×10^{-6}
O_2	2.5×10^{-7}	8.9×10^{16}	370	2×10^{-5}
AsF_5	1×10^{-4}	2.2×10^{18}	190	3×10^{-4}

tial greater than 0.3 V, the I-V characteristic becomes linear indicating that the device resistance is now dominated by the roughly 3 kΩ bulk resistance of $(CH)_x$. Below 0.3 V, extrapolation of the linear part of Fig. 4(b) to zero bias yields a saturation current density $J_S = 5.4\times10^{-6}$ A/cm^2. If we assume the standard thermionic emission model of a Schottky junction,[10] the dependence of the current density on bias voltage and junction parameters is given by

$$J = J_S e^{qV/nkT}, \tag{1}$$

where

$$J_S = A^* T^2 e^{q\varphi_b/kT}, \tag{2}$$

and

$$A^* = 4\pi q m^* k^2/h^3. \tag{3}$$

Assuming $m^* \sim 1$, $A^* = 120$ A/°K^2 cm^2, we find at room temperature the barrier height $\varphi_b = 0.74$ V. Note that φ_b is quite insensitive to the choice of m^*. Finally, Fig. 5 demonstrates that aluminum forms a blocking contact to undoped *trans*-$(CH)_x$. The I-V characteristic is very similar to that for indium on undoped *trans*-$(CH)_x$.

In order to gain further insight into the junction properties, we measured the variation of its capacitance with reverse bias. Simple depletion layer theory yields the following expressions for this dependence[11]:

$$C = \varepsilon\varepsilon_0 A/d, \tag{4}$$

where

$$d = [2\varepsilon\varepsilon_0(\psi_0 + V_R)/qN_A]^{1/2}. \tag{5}$$

Here ψ_0 is the built-in potential, V_R is the reverse bias, and

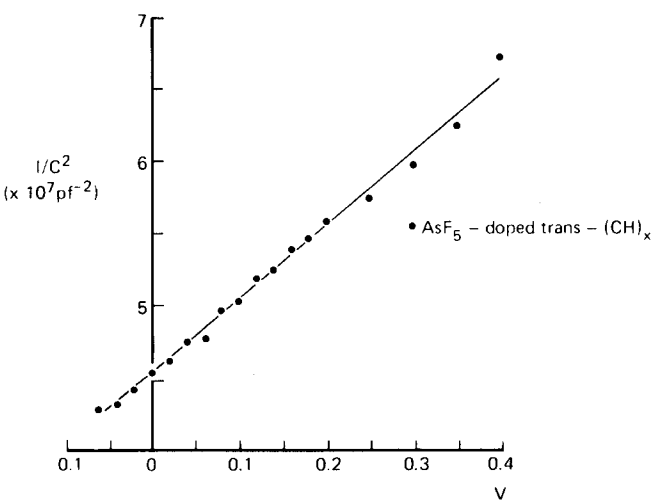

FIG. 6. C-V characteristic of a lightly AsF_5-doped In/*trans*-$(CH)_x$ junction.

N_A is the ionized acceptor/trap concentration. We designate N_A as the combined acceptor/trap concentration given the relatively low purity of undoped $(CH)_x$. It is readily seen that the slope of a $1/C^2$ vs V_R plot gives the acceptor/trap concentration and the V_R intercept gives the built-in potential. Knowing N_A and σ then enables one to determine the mobility for a given doping level. The measurement of junction capacitance by ac techniques on $(CH)_x$ must be approached with some caution, as pointed out by Grant and Krounbi.[8] They showed that the complex impedance of a $(CH)_x$ Schottky junction could display a spurious frequency dependence due to the high series resistance introduced by the $(CH)_x$ bulk as discussed above. Thus, for each sample, a proper choice of modulation frequency must be made. In all our measurements, the modulation frequencies (100–1000 Hz) were low enough to ensure that only the true junction capacitance was detected. Figure 6 shows the results for one of our AsF_5-doped samples. Analysis of the slope and intercept for these data yields $d \approx 190$ Å, $\psi_0 \approx 0.9$ V, and $N_A = 2.2\times10^{18}$ cm^{-3}. Assuming complete thermalization of the acceptor/trap concentration and $\sigma = 10^{-4}\,\Omega^{-1}$ cm^{-1}, we find 3×10^{-4} cm^2/V sec for the hole mobility. Table II summarizes the results for this and the other samples.

We now discuss the overall implications of both the I-V and C-V characteristics as a function of doping. Table III contains the junction parameters obtained by analyzing these characteristics for the AsF_5 doped sample shown in Fig. 4. Salanek *et al.*,[12] using photoemission techniques, have measured the work function of semiconducting $(CH)_x$ to be 4.5 eV. We believe this value to apply to our samples due to their relatively light doping levels. With this number, and a band gap of 1.48 eV as determined from photovoltaic measurements, we find the electron affinity of $(CH)_x$ to be $\chi \approx \varphi_s - E_G = 3.0$ eV. The value 4.5 eV for the $(CH)_x$ work function also agrees well with the finding that gold forms an ohmic contact while indium and aluminum are blocking. On the other hand, an estimate of the barrier height $\varphi_b = E_G - (\varphi_{\text{In}} - \chi)$ yields 0.4 eV, considerably different from the value 0.72 eV obtained from the saturation current based on the thermionic emission model. Moreover, both values of φ_b are smaller than the built-in potential as determined from C-V measurements. When trying to interpret

TABLE III. Junction parameters for an AsF_5-doped In/*trans*-$(CH)_x$ Schottky barrier.

n	J_S(A/cm^2)	φ_b(V)	ψ_0(V)
1.98	5.4×10^{-6}	0.74	0.9

these data in the context of simple Schottky models, one must remember that we are dealing with a matted fibril structure for which the concept of an intimate contact in the traditional metal-semiconductor sense is whimsical in the extreme. The difficulties involved are indicated by the value of the ideality parameter $n = 1.98$. Departures from the theoretical $n = 1$ are often caused by extensive recombination activity in the depletion region. Under such conditions, the thermionic emission model cannot be used to analyze for the barrier height.[13] Even in those Schottky junctions where $n \approx 1$ it is often found that φ_b is independent of the metal used for the contact. In actuality, surface states have a profound effect on the properties of practical Schottky barriers and strongly affect the position of the Fermi level relative to the metal and semiconductor band edges. We have no reason to believe otherwise for $(CH)_x$ Schottky junctions. Nonetheless, because surface states and image forces modify ψ_0 and φ_b, in the same way, it is interesting to speculate on our observation that $\psi_0 > \varphi_b$. One possible explanation is that the portion of the $(CH)_x$ in actual contact with the indium is degenerate. This conjecture would concur with the suggestion that metallic regions exist in $(CH)_x$ even in the semiconductor regime.[14] However, given that our blocking contact was underneath the film on the substrate, it seems unlikely that enough AsF_5 could have penetrated sufficiently deep to chieve metallic doping levels. For the present, we must conclude that finding $\psi_0 > \varphi_b$ is further evidence that something beyond simple Schottky theory is needed to describe blocking contacts on $(CH)_x$.

As seen from Table II, the mobility magnitudes are very small and concentration dependent, increasing with increasing dopant amounts. These findings are in general agreement with Park *et al.*[15] who used direct analysis of conductivity data as a function of dopant concentration to obtain mobility. Yet from elementary considerations based on band theory one would conclude that the hole mobility should be of order 1 cm^2/V sec and independent of concentration. Several models suggest themselves as reasons for the observed behavior:

(1) In several highly disordered covalent semiconductors, such as amorphous and polycrystalline silicon, anomalously low and concentration dependent mobilities are also observed.[16] Such systems have a relatively high density of localized states in the forbidden gap which tend to trap and scatter carriers at low concentrations. As carrier concentration increases, these localized states fill up until none are left and additional carriers begin to occupy the more extended band states. Thus, one observes a rather sudden increase in mobility at some critical carrier density.

(2) Concurrently, the net mobility could arise as an average over various inhomogeneous dopant distributions. For example, if each fiber were oxidized radially from the outside in, the resulting mobility would be the average of the highly conducting sheath and the insulating interior.

(3) On the other hand, Park *et al.*[15] have proposed diffusive hopping of charged solitons as the principal transport mechanism in lightly doped *trans*-$(CH)_x$. Our data, although consistent with this picture, should not be considered direct evidence for solitons given the above alternatives.

In performing our measurements under reverse bias, we noticed a gradual decrease in back resistance with time. That is, over a period of 1 h or longer, depending on the doping level, our junctions lost much of their rectifying property. This decrease in resistance was more pronounced the higher the doping level. After returning to zero bias for a roughly equivalent period, normal junction properites returned. The most pausible explanation for this behavior is that negative charge is leaking into the depletion region as a function of time under reverse bias. The most obvious source of negative charge is the dopant anion. If these anions are weakly bound to the host polymer chain, it is quite possible that they could also undergo slow migration in an externally applied field.

In conclusion, we have shown that rectifying junctions can be obtained by contacting low work function metals to lightly doped *trans*-$(CH)_x$. Furthermore, these junctions display overall I-V and C-V characteristics expected from general Schottky barrier theory. On the other hand, detailed analysis indicates serious departures from the simple Schottky model and further studies will be necessary for more complete understanding. Combining bulk conductivity measurements with carrier concentrations derived from the junction C-V characteristics results in a concentration dependent mobility, a perhaps not unexpected finding given the highly disordered state of the host polymer. Finally, from a device application point of view, the relatively small back-to-forward resistance ratio and reverse characteristic degradation with time present significant future material and device fabrication challenges that remain to be addressed.

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