

PHOTOCONDUCTIVITY AND JUNCTION PROPERTIES OF POLY-ACETYLENE FILMS*.*.*

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Summary

Photoconductivity and photovoltaic effects of AsF₅-doped and undoped *trans*-(CH)_x films have been measured at room temperature in the wavelength region from 0.3 to 3.5 μm. The photovoltaic response threshold at 1.48 eV, measured on Schottky barrier junctions with a low work function metal, is interpreted as the single particle band-gap of *trans*-(CH)_x. I-V and C-V characteristics of the junctions indicate that good Schottky barriers are formed between lightly doped p-type (CH)_x and low work function metals. Evidence for $\sim 2 \times 10^{18} \text{ cm}^{-3}$ deep traps in both doped and undoped *trans*-(CH)_x is obtained from analysis of these characteristics.

Introduction

The considerable recent interest in the electronic properties of (CH)_x has largely concentrated on highly doped material showing metallic conductivity [1 - 6]. The intrinsic and semiconducting properties of (CH)_x in the undoped and lightly-doped state have not been extensively investigated. In this paper we report on studies of photoconductivity and photovoltaic effects and on the properties of Schottky barriers formed with lightly AsF₅-doped *trans*-(CH)_x in contact with low work function metals. From the phototransport experiments we have obtained the first definitive measure of the single particle energy gap in *trans*-(CH)_x [7]. Studies of the junction properties show that well-defined Schottky barriers are formed and demonstrate the presence of a high density of deep trapping levels which play a strong role in determining the junction profile.

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Experimental

All measurements were made on films of thermally isomerized *trans*-(CH)_x in either the undoped condition or lightly doped by exposure to AsF₅ gas. (CH)_x films were deposited on sapphire substrates. Ohmic contacts for photoconductivity cells and for one side of the junction cells were obtained with evaporated Au films. The Schottky barriers were obtained by evaporation of a semitransparent low work function metal (In, Al) on which the (CH)_x film was deposited. All sample handling was carried out in the inert atmosphere of a dry box with the exception of very short air exposure during contact evaporation procedures.

Results

A detailed account of the phototransport experiments has been published elsewhere [7]. In this paper we will only briefly review the central results. Figure 1 shows the photovoltaic response curve obtained for an In/

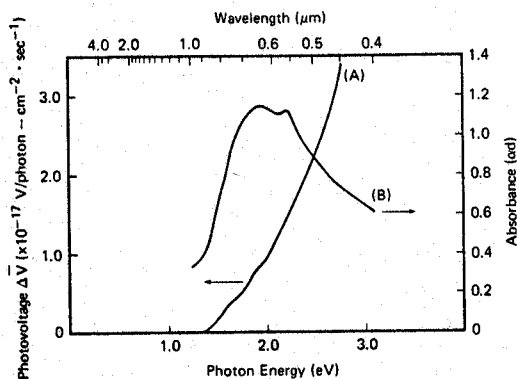


Fig. 1. (A) Open-circuit photovoltaic response normalized to the incident photon flux and transmittance of the In Schottky barrier contact. (B) Absorbance spectrum of undoped *trans*-(CH)_x.

trans-(CH)_x Schottky barrier illuminated through the semitransparent In metal. These data replotted as the square of the photovoltage *versus* photon energy show a distinctive threshold at 1.48 eV. The onset of the photovoltage is observed to coincide closely with the optical absorption edge. Similar results have been obtained with several other samples with the (CH)_x conductivity ranging from $2.6 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ to $4 \Omega^{-1} \text{ cm}^{-1}$. The photovoltaic threshold is independent of doping level, which supports our belief that 1.48 eV is the single particle band gap in *trans*-(CH)_x. Internal photoemission from the In into (CH)_x cannot be completely eliminated as the source of the observed threshold; however, Fowler plots of these data are

not linear as would be expected for photoinjection. The 1.48 eV threshold is in fair agreement with the 1D band structure calculations of Grant and Batra [8]. In these calculations the energy gap was found to be very sensitive to the degree of bond alternation, varying between 0.9 eV for bond lengths chosen from β -carotene to as much as 2.3 eV for completely conjugated bonds. Thus bond alternation in $trans$ -(CH)_x is probably intermediate between uniformity and complete conjugation.

Photoconductivity measurements on undoped $trans$ -(CH)_x were similar for both planar and sandwich sample configurations using Au for all electrodes. The photoconductivity showed a peak at 1.35 eV followed by a steep rise in photocurrent at higher proton energies roughly similar to the photovoltaic response. The quantum yield was typically 3×10^{-8} carriers/absorbed photon. The origin of the peak at 1.35 eV is not understood at this time. It may be due to an extrinsic electronic state or it may represent dissociation of weakly bound excitons.

As part of the evaluation of the junctions on which the photovoltaic measurements were made, the I - V and C - V characteristics were obtained. These measurements were felt to be very important in establishing whether these junctions could be assumed to be simple Schottky barriers or whether a more complex junction profile existed which might complicate interpretation of the photovoltaic effect. Figure 2 shows the I - V characteristic obtained for an In/(CH)_x junction. Points to be observed on this I - V characteristic are the good rectification properties, the linear regions at large forward bias, which is in good agreement with the bulk resistance of the (CH)_x for this level of doping, and the apparent barrier height of 0.32 eV.

Capacitance *vs.* voltage, C - V , measurements were made on these junctions over the frequency range 5 - 500 kHz. Some of these results are shown in Fig. 3 for an In/(CH)_x junction. For a simple Schottky barrier device, a linear $1/C^2$ *vs.* V plot implies uniform doping in the junction region with the slope being a measure of the ionized dopant concentration. The intercept on the forward bias axis is a measure of the barrier. The frequency dependence seen in Fig. 3 has some effect on the apparent slope of the linear reverse bias

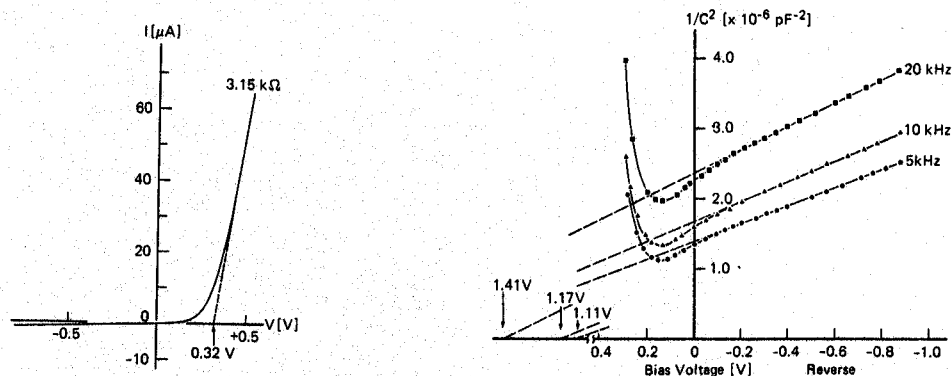


Fig. 2. I - V characteristic of a lightly AsF_5 doped $trans$ -(CH)_x junction with In.

Fig. 3. $1/C^2$ *vs.* bias voltage at several frequencies for the In/ $trans$ -(CH)_x junction of Fig. 2.

regime, and a very strong effect on the apparent barrier height obtained from the forward bias intercept. Similar frequency dependence has been studied in Schottky barriers formed with III - V and II - VI compounds in which deep levels coexist in the forbidden gap with shallow donor or acceptor levels [9, 10]. The frequency dependence arises from the long relaxation times associated with these deep centers whose population changes in the strong band bending region associated with the Schottky barrier.

Discussion

In this paper we can only summarize the results of these investigations. A more extensive treatment of the junction properties will be presented elsewhere [11]. To analyze the frequency dependent C - V data we have adopted the theory of Perel and Éfros [12]. In their treatment the capacitance of the junction is

$$\frac{1}{C(\omega)} = \frac{1}{C_0} + \eta(\omega), \quad (1)$$

where C_0 is the usual low frequency limit capacitance of the junction and the frequency dependent term is expressed as

$$\eta(\omega) = \frac{\pi^3 \omega \tau_1 kT}{8e^2 \epsilon N_T}, \quad (2)$$

for the case where there is a sufficiently high concentration of ionized deep impurities. Here ω is the frequency, τ_1 is the relaxation time of the deep impurity population in the junction region, ϵ is the dielectric constant and N_T is the concentration of deep impurities.

Schottky barrier theory predicts that $1/C(\omega)$ will be linear in $V^{1/2}$ for high reverse bias and will have intercept $\eta(\omega)$ at zero bias. We have analyzed the data of Fig. 3 in this way to obtain the value of $\eta(\omega)$ for each curve. All the frequency data can then be replotted in the reduced form $(1/C(\omega) - \eta(\omega))^2$ vs. voltage and are found to be on a single straight line. From the slope of this plot the total concentration of deep levels and shallow acceptors $N_T + N_A$ is deduced to be $2.5 \times 10^{18} \text{ cm}^{-3}$ where $\epsilon = 5$ has been assumed from dielectric function measurements on undoped $(\text{CH})_x$ [11]. From the film conductivity ($8.4 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$) and the assumption that the conductivity mobility $\mu \approx 1 \text{ cm}^2/\text{V s}$ [1], the shallow acceptor density $N_A = 5 \times 10^{16} \text{ cm}^{-3}$ in this sample. Thus the deep level concentration $N_T = 2.5 \times 10^{18} \text{ cm}^{-3}$. The intercept of this reduced plot is at 0.16 V. Using this intercept together with the barrier height of 0.32 eV obtained from the I - V characteristic allows us to estimate that the deep levels are about 0.16 eV above the Fermi level. The relaxation time τ_1 can also be estimated to be $\approx 10^{-2} \text{ s}$ from the values of $\eta(\omega)$ determined at each frequency.

It is interesting to note that interface states do not appear to play a strong role in determining the profile at $(\text{CH})_x$ /metal junctions. Gold with a work function $\phi_{\text{Au}} = 5.1$ eV forms an ohmic contact with *trans*- $(\text{CH})_x$, while In with work function $\phi_{\text{In}} = 4.2$ eV forms a Schottky junction with a 0.32 eV barrier for holes. In the absence of surface states one can predict the type of band bending and the approximate barrier height from the difference between the metal work function ϕ_m and the semiconductor electron affinity χ_{sc} , assuming that the band gap, E_g , and position of the Fermi level, E_F , are also known. The electron affinity of $(\text{CH})_x$ can be estimated from the photoemission threshold at 4.7 eV of Salaneck *et al.* [13]. Using our value of $E_g = 1.48$ eV the electron affinity is about 3.2 eV. For p-type $(\text{CH})_x$ in contact with In the maximum barrier is therefore $E_g - (\phi_M - \chi_{\text{sc}}) \approx 0.5$ eV. This barrier will be reduced by the energy of the Fermi level above the valence band edge, in reasonable agreement with the 0.32 eV barrier we have measured. On the other hand, contact with a larger work function metal such as Au ($\phi_{\text{Au}} = 5.1$ eV) must always result in a hole injecting junction since $\phi_M - \chi_{\text{sc}}$ is larger than E_g . This conclusion is experimentally verified by the fact that ohmic contact to both doped and undoped $(\text{CH})_x$ is readily achieved with both Au and Pt [6, 7].

Conclusion

In summary, phototransport experiments yield a value of 1.48 eV for the single particle band gap in *trans*- $(\text{CH})_x$. This value of the band gap is found to be independent of AsF_5 doping level for a conductivity range from 2.6×10^{-4} to $4 \Omega^{-1} \text{cm}^{-1}$. Schottky barriers of lightly AsF_5 -doped *trans*- $(\text{CH})_x$ in contact with In have been characterized and the major junction parameters evaluated. Frequency dependent C-V characteristics show that a high density ($N_T = 2.5 \times 10^{18} \text{cm}^{-3}$) of deep levels, about 0.16 eV above E_F , exist in both the undoped and AsF_5 -doped *trans*- $(\text{CH})_x$.

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Note added in proof

We have recently re-analyzed the frequency dependence of our In/trans-(CH)_x Schottky barriers and now find it to be in large part due to the resistance of the bulk of the sample which is in series with the parallel RC circuit of the junction. This equivalent circuit yields an apparent frequency dependence even if the junction properties are non-dispersive. Thus, although there may be some frequency dependence arising from deep traps according to the model used in this paper, it now appears that the junctions approximate ideal Schottky barriers more closely than previously believed. Detailed data and analyses will be presented in ref. 11.