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Formation of a Schottky barrier between eutectic Ga,In and thiophene oligomers

E. J. Lous,[a] P. W. M. Blom, L. W. Molenkamp,[b] and D. M. de Leeuw

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The formation of a Schottky barrier between an eutectic (Ga,In) alloy and a highly doped thiophene oligomer is followed as a function of time using current density–voltage and capacitance–voltage measurements. Within 1 h, the diode characteristics change from almost nonrectifying, leaky behavior into a rectification ratio of 10^4 with a considerably reduced leakage current. Measurements and energy band diagram calculations show that the depletion width increases with time due to a decrease in the ionizable acceptor density of the semiconductor at the Schottky interface. This is probably caused by a chemical reaction between the in-diffusing metals and the doped oligomer. © *1997 American Institute of Physics.* [S0021-8979(97)05308-5]

INTRODUCTION

Many conjugated organic materials show semiconductive properties. In recent years several types of devices employing these properties such as diodes, field effect transistors (FETs), and light emitting diodes (LEDs) have been investigated.[1,2] An important class among the amorphous organic semiconductors is the thiophene oligomers, which are stable *p*-type semiconductors. Thin-film diodes have been made by sandwiching thiophene oligomers between a low-work-function metal such as In, Ag, Al, Pb, and Sn, and an ohmic contact such as Au.[3–8] Such diodes exhibit rectification ratios of 10^4–10^6 (measured between drive voltages of +1 and −1 V) and quality factors *n* in the range of 1.2–2. These specifications compare favorably with diodes made from amorphous Si.[9] The switching speed of the organic diodes can be improved from less than 100 Hz to about 10 kHz, by doping of the semiconductor to a high acceptor density of about 10^{20} cm^{-3}. Actually, it is a surprising result that well-rectifying Schottky diodes can be obtained from such highly doped semiconducting films.[7,8] For these high dopant concentrations one expects an extremely thin depletion width of less than 10 Å. For such thin barriers tunneling current transport processes should result in an ohmic, nonrectifying behavior at the Schottky contact.

In previous articles we have shown that using indium as the Schottky contact on both unintentionally doped and highly doped (5%) thiophene oligomers, a thin interface layer is present between the indium Schottky metal and the semiconductor bulk layer.[7,8] The interface layer has been characterized as a partially *undoped semiconducting* layer with a low ionizable acceptor density, N_A (p^- layer). This density is at least one order of magnitude lower than that in the bulk layer of the semiconductor (p^+ layer). The p^- layer enables the well-rectifying behavior of the Schottky diodes. This rectifying behavior does not occur at the p^-/p^+ junction but at the Schottky metal/p^- layer interface; however, the p^- layer also exhibits a low conductivity and, therefore,

also limits the forward current of the diodes. The effective undoping of the interface layer is presumably caused by the fabrication process, e.g., evaporation of the indium on top of the thiophene film. A chemical reaction is induced between the indium and the oligomer. This interpretation is supported by ultraviolet photoelectron spectroscopy measurements for aluminum evaporated on the thiophene oligomer α-sexithiophene.[10]

In this article we report on time-resolved measurements on the formation of a rectifying barrier between a thiophene oligomer layer and an eutectic Ga,In alloy as Schottky contact. The formation of the barrier is slow enough to allow a full set of current-density–voltage (J–V) and capacitance–voltage (C–V) measurements. Eutectic Ga,In is a liquid metal, which has about the same work function (4.1–4.2 eV) as In (4.12 eV) and should result in a similar barrier height.[11] The advantage of Ga,In devices is that no metal evaporation during the fabrication process is needed. Hence, temperature accelerated reactions and temperature induced dedoping (for example by decomposition, separation, etc., of film surface materials) are circumvented. In our Ga,In devices we find (at room temperature) a changeover with time from an ohmic contact to a Schottky-type behavior. This changeover occurs at a time scale of several hours, probably due to a chemical reaction between in-diffusing metal atoms and the thiophene oligomer molecules. Eventually, with eutectic Ga,In similar or even better rectifying diodes are obtained than with evaporated In as Schottky contact.[7,8]

MATERIALS AND METHODS

Doped semiconducting films of α,α'-coupled dodecathiophene, substituted with four *n*-dodecyl side chains at the thiophene rings 2, 5, 8, and 11 ($T_{12}d_4$) (obtained from Syncom B.V., University of Groningen, The Netherlands) have been prepared as reported earlier.[7,12] In short: $T_{12}d_4$ has been doped in dry tetrahydrofuran (THF) (Merck, pro analysis, and refluxed, for 1 h over a sodium-potassium melt, prior to use) with a dry-THF solution of 2,3-dichloro-5,6-dicyano-1,4-benzo-quinone (DDQ) (British Drug House, 98%). The doping level is defined as the percentage of donated holes

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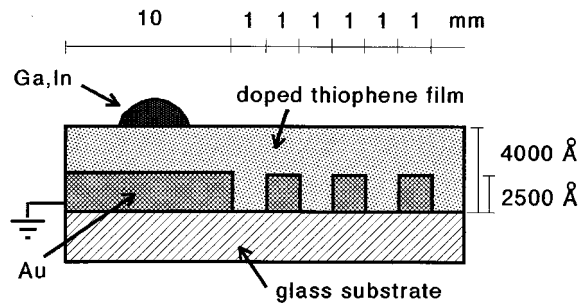
FIG. 1. Schematic diagram of the device structure.

RESULTS

As a typical example, we show in Fig. 2 the $J-V$ dependence of a device consisting of a Ga,In contacted, 8% doped $T_{12}d_4$ film, after time intervals of 2 min, 1 h and 1 day. Initially, we observe a leaky diode. The $J-V$ dependence is characteristic of a diode with a parallel resistor R_p both in series with a resistor R_s (see inset of Fig. 2),[13]

$$J = J_0 \left[\exp\left(\frac{q}{nk_BT} (V_b - JR_s) \right) - 1 \right] + \frac{(V_b - JR_s)}{R_p}, \quad (1)$$

where V_b is the externally applied bias voltage, q the elementary charge, k_B the Boltzmann constant, and T the temperature. R_s and R_p are in units of $\Omega\,cm^2$. The part of the $J-V$ curve at low (forward) voltage at which J_F overlaps with the J_R trace is a measure of the diode leakage. Here the total current is dominated by the (leakage) current through R_p. (Note that $R_s \ll R_p$.) The decrease of the diode leakage current with time is due to an increase in R_p (from about 4 $k\Omega\,cm^2$ to 3 $M\Omega\,cm^2$) and is observed by a decrease in the reverse current density. Initially the change in R_p is fast ($\tau \approx 6$ min). After about 1 h the rectification at $+1/-1$ V has increased to about 10^4 [Fig. 2(b)]. Then, R_s and R_p change about equally slowly ($\tau \approx 160$ min). R_s limits the forward current density J_F of the diode, which is considerably smaller than the *bulk limited* forward current densities.[7] These are calculated from the bulk conductivity measured before and after the experiment, using the bottom Au contacts and are shown in the top of Figs. 2(a) and 2(c). Clearly, the change in bulk conductivity is negligible, implying no degradation of the bulk film due to atmospheric influences

per thiophene ring. Each DDQ molecule can accept two electrons; hence, a doping level of 1% corresponds to a hole density of about $9 \times 10^{19}\,cm^{-3}$.

Devices have been fabricated by spin-coating films (typical thickness: 4000 Å) on glass substrates provided with four evaporated Au stripes and a large Au contact area (Fig. 1). Au is an ohmic contact to (doped) $T_{12}d_4$ and is used as bottom electrode in our diodes. Our device layout thus allows for both a measurement of the bulk conductivity and of the diode characteristics on the same device. Small droplets of liquid Ga,In (16.5 at. % In) with typical contact areas of $2.5 \times 10^{-3}\,cm^2$ have been deposited on the thiophene film and used as top contacts. Due to the unknown wetting properties of the eutectic Ga,In droplet the area uncertainty is estimated to be 20%. This error is, however, for the determination of the Schottky barrier heights and for the energy band diagram calculations within the scope of this study of negligible influence. For time-dependent studies the moment of contact between the droplet and the film is taken as time zero. The setup for measuring the $J-V$ and the $C-V$ data

FIG. 2. The figure shows the current density as a function of bias voltage for a 8% doped $T_{12}d_4$ film (thickness 4700 Å) on which, at time zero, an eutectic Ga,In contact is placed. Curves are taken after (a) 2 min, (b) 1 h, and (c) 1 day, respectively. The decreases in both the forward and reverse currents are much faster than the decrease in bulk conductivity of the film, shown as the expected bulk limited J_F by both upper ohmic traces between 1 and 2 V in (a) and (c). The inset in (a) shows the dc equivalent circuit for the diode.

FIG. 3. The quality factor n of the diode vs the duration of contact between the eutectic Ga, In Schottky contact and the 8% doped $T_{12}d_4$ film.

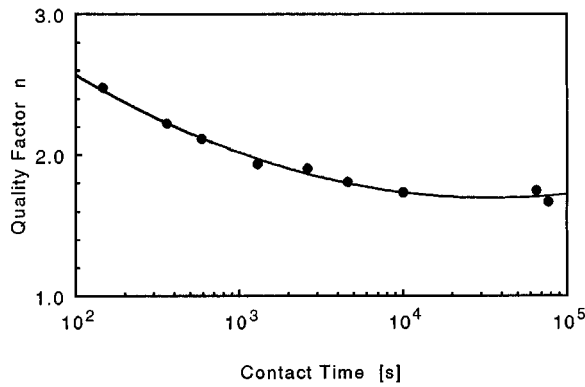FIG. 5. From the same data set shown in Fig. 4 (area/capacitance)^2 vs bias voltage is calculated assuming a parallel $R-C$ circuit, as the ac equivalent circuit for the reversed biased diode. Shown are the data after (∇) 20 s, ($\triangle$) 9 min, ($\bigcirc$) 7 h, which curves are 4 times magnified in the figure (right-hand scale), and (+) 8 days (left-hand scale), respectively, after contacting. The lines represent the slopes from which N_A is deduced.

during the series of $J-V$ measurements. Therefore, we tentatively attribute the observed changes with time of the diode $J-V$ characteristics, to changes in the metal–oligomer interface. The quality factor n is determined from the steep exponential slope of J_F in Fig. 2, starting from the voltage at which J_F deviates from J_R. In Fig. 3 it is shown that the quality factor decreases from 2.5 to 1.7 with increasing contact time. The current density at zero bias J_0, found by extrapolation of the above-mentioned exponential slope, changes from about 1.6×10^{-8} to 6.3×10^{-11} A cm^{-2}. Assuming conventional thermionic emission theory, we find that the Schottky barrier ϕ_b changes from about 0.86 after 2 min to 0.96 after 1 h to 1.0 eV in 1 day.[13] These values may

deviate from the *full* Schottky barrier height ϕ_{b0} by a possible image force barrier lowering effect $\Delta\phi$: $\phi_{b0} = \phi_b + \Delta\phi$. At high forward bias, beyond 1 V, J_F depends superlinearly on the voltage; $J_F \propto V^y$, where $y \approx 2.5$. This is indicative of a space-charge-limited-current transport mechanism through the low-conductivity metal–oligomer interface layer.[14]

In Fig. 4 we show the time dependence of the absolute impedance $|Z|$ and the phase θ of the diode, as a function of the bias voltage, measured at a modulation frequency of 1 kHz. From $|Z|$ in Fig. 4(a) we observe that at all times rectification occurs, while the $|Z|$ curves as a whole shift to higher impedance with time, in agreement with the total shift of the $J-V$ curve in Fig. 2 toward lower current density. This effect in both J_0 and $|Z|$ cannot simultaneously be explained by a drastic change in time of the Ga,In contact area. Therefore, based on similar J_0, $|Z|$, and barrier height values, we assume that the contact area is well comparable with those of evaporated In contacts.[7,8] The phase [Fig. 4(b)] exhibits especially large changes with time and is informative for the understanding of the time dependence. At high forward bias the phase is all the time close to zero and the device behaves as a resistor. However, for small reverse bias the phase changes in time from close to zero (20 s) to $-90°$ (7 h); i.e., from a resistive to a capacitive behavior. This reflects an increase of the width of the depletion layer with a simultaneous decrease of (tunnel) leakage currents. For high reverse bias, however, these leakage currents again start to dominate the transport through the depletion region and cause the phase to go back to zero.

The impedance data of Fig. 4 are used to determine the change in capacitance of the diode as a function of bias voltage. From a plot of (area/capacitance)^2 versus bias voltage V_b, as shown in Fig. 5, the built-in voltage V_{bi} can be determined from the intercept of the capacitance data with the voltage axis at low V_b. As the reverse current density becomes less dominated by R_p in time, standard Schottky theory becomes more valid as the requirement of a parallel $R-C$ circuit is reached. At longer contact times, V_{bi} remains
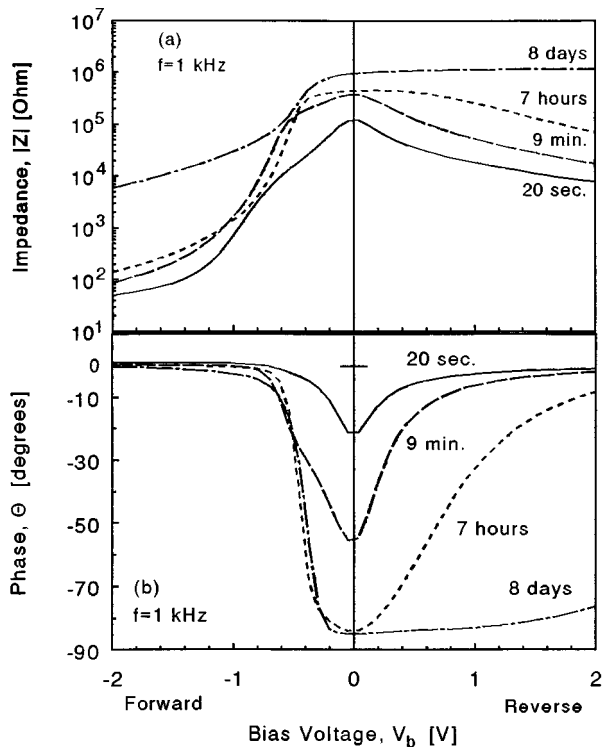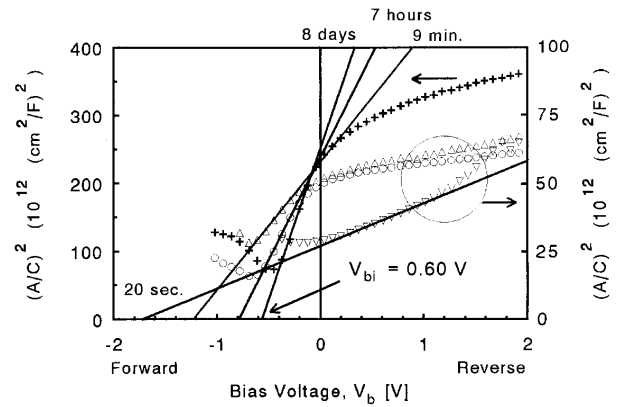

FIG. 4. The (a) impedance $|Z|$ and (b) phase θ as function of bias voltage at 20 s, 9 min, 7 h, and 8 days after the contact between the eutectic Ga,In alloy is made with a 7% doped $T_{12}d_4$ film (thickness 4600 Å). The contact area is 2.5×10^{-3} cm^2, frequency 1 kHz, and oscillation amplitude 0.1 V.
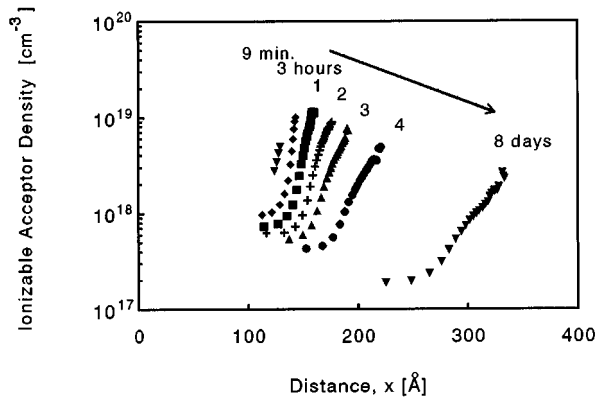
FIG. 6. The ionizable acceptor density N_A as function of the depletion depth x of the diode, calculated from the same set of data as partly shown in Figs. 4 and 5. The shown profiles are at (▼) 9 min, (◆) 3 h, (■) 1, (+) 2, (▲) 3, (●) 4, and (▼) 8 days after contacting the Ga,In to the film.

unchanged at 0.6 V. This change in V_{bi} is also seen in the $J-V$ data of Fig. 2, as a shift of the voltage at which J_F starts to saturate (which is also an indication for V_{bi}) to smaller values. The limiting value for V_{bi}, 0.6 V (8 days after contact) from Fig. 5 agrees well with the built-in voltage deduced from Fig. 2(c) (see also Fig. 4 of Ref. 7). Previously, $V_{bi} \approx 0.5-0.6$ has also been observed for devices with evaporated In contacts.[7,8] In addition we note that the saturation of the curves in Fig. 5 at high reverse bias voltage ($V_b \approx 2$ V) is typical for diodes with graded dopant profiles.[15]

From the same $C-V$ data of which a sample is shown in Figs. 4 and 5 we have calculated the profile of the ionizable acceptor density N_A as function of the distance x to the Ga,In metal–oligomer interface. In Fig. 6 these profiles are shown for 9 min, 3 h, 1, 2, 3, 4, and 8 days after contact is made. For each profile only those data points are shown that fulfill the assumption of a parallel $R-C$ model as used in standard Schottky theory. The profiles of the ionizable acceptor density show a steep gradient of more than one order. The gradient separates a partially undoped p^- layer at the Schottky metal side from the highly doped bulk semiconductor film (p^+ layer). The actual dopant concentration of the bulk of 6×10^{20} cm^{-3} is not reached at 2 V reverse bias. This may imply that not all the dopants were ionized. Below we show that, in a similar manner to that for In contacts, the density profile of the interfacial p^- layer must be relatively flat.

The time dependence of the ionizable acceptor density profile of Fig. 6 is as follows: At short contact times the depletion width is small and large tunnel currents cross the barrier. Hence the phase of the impedance [Fig. 4(b)] is close to 0°. With increasing contact time the p^- layer becomes thicker and, due to the decrease of the ionizable acceptor density in the p^- layer from about 10^{18} to 10^{17} cm^{-3}, also less conductive. This is consistent with the observed decrease in J_F with time (see Fig. 2), since the low-doped p^- layer limits the forward current density of the diode, and is interpreted as the R_s part of the equivalent circuit. Starting with a width of the depletion layer of less than 100 Å, sufficiently thin for tunneling to occur, the increase of this width is reflected by the phase change of the impedance from 0° to
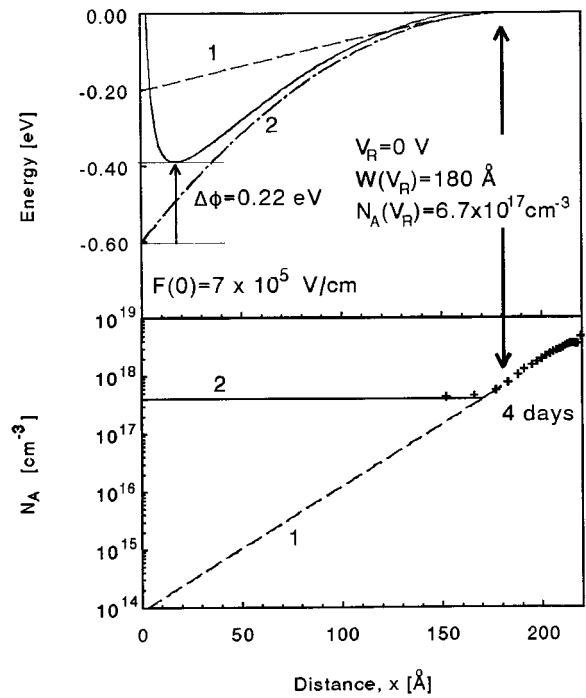

FIG. 7. The bottom part shows the $N_A(x)$ profile after 4 days, selected from Fig. 6. The p^- layer extends from the metal–oligomer interface at the origin ($x=0$) up to $x=180$ Å, where the gradient starts. The numbers 1 and 2 indicate two possible extrapolations of $N_A(x)$ toward the Schottky metal–oligomer interface. The corresponding calculated band-bending diagrams are shown in the top part. Only profile 2 has sufficient band bending at $x=0$ to yield the built-in voltage of $V_{bi} = 0.6$ V that is found experimentally. The solid line is the band bending due to profile 2, after including the effect of the image force, which causes a barrier lowering of $\Delta\phi=0.22$ eV. Note: The potential energy scale on the vertical axis is shifted by ($\phi_{b0} - qV_{bi}$).

−90° (Fig. 4) and leads to the increase of the Schottky barrier and of the rectification of the diode (Fig. 2). The observed changes with time are probably due to the occurrence of a chemical reaction between the Schottky metal and the doped oligomer film, leading to a partially dedoped interfacial p^- layer.

DISCUSSION

Information on the N_A profile in the p^- layer is obtained from a calculation of the band bending in the device, which we now explain. We focus on the slowly changing experimental N_A profile as obtained after 4 days and shown in Fig. 6 and in more detail in the bottom part of Fig. 7. In Fig. 7 we indicate for the p^- layer two possible extended N_A profiles (1 and 2), which represent different extrapolations from the data points toward the metal interface; profile 1 is a logarithmic-linear extrapolation of the experimental data points for distances x larger than 180 Å, toward the Schottky metal interface, profile 2 is as profile 1, while in addition a constant, minimum density of $N_A = 4 \times 10^{17}$ cm^{-3} is assumed. For these profiles we calculate the corresponding potential energy of the valence band $V(x)$ by solving the Poisson equation,

$$-\frac{\delta^2 V(x)}{\delta x^2} = \frac{\delta F(x)}{\delta x} = \frac{\rho(x)}{\epsilon_s} = \frac{qN_A(x)}{\epsilon_s}, \quad (2)$$
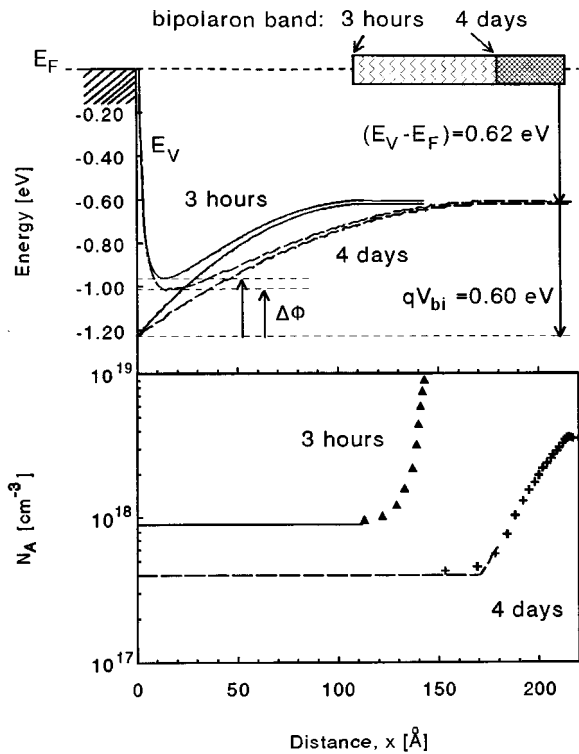
FIG. 8. The bottom part shows two $N_A(x)$ profiles of Fig. 6, taken after 3 h and 4 days. Their corresponding energy band diagrams are shown in the top part by the lines that have the $x=0$ axis as asymptote, reflecting the contribution of the image force. The two other lines show the band bending as calculated from the Poisson equation. These two lines show that the full Schottky barrier height stays constant with time, while the image force barrier lowering decreases and the depletion width increases with time. The position of the hole bipolaron band is indicated. Note that this state cannot exist in the charge free depletion region of the device, as is schematically drawn for $V_b=0$ V, and which broadens with time (see Ref. 8).

with F the electric field, ρ the charge density, and ϵ_s the dielectric constant of the semiconductor. In this figure we use boundary conditions $[V(0) = -V_b$, $V(w) = 0$, and $F(w)=0]$ which are appropriate for easy comparison of the magnitude of band bending of both profiles. [To obtain the absolute scale for the complete energy diagram, the voltage scale needs to be shifted upward by $(qV_{bi}-\phi_{b0})/q$.] As deduced from the $C-V$ and $J-V$ data (see also Fig. 4 of Ref. 7) the total band bending at the Schottky interface (at $x=0$), which is qV_{bi}, should equal about 0.6 eV. The total band bending at $x=0$ that is calculated for profile 1 ($qV_{bi} \approx 0.20$ eV) is far too small, which thus excludes profile 1. For profile 2 sufficient band bending, i.e., 0.6 eV, is found.[8] Note that also when assuming a constant profile as in profile 2, the amount of band bending is very sensitive to the magnitude of N_A. If the N_A level of profile 2 is reduced by only a factor of 4, the calculated qV_{bi} drops to 0.26 eV. This means that our calculations enable a quite accurate determination of the actual doping profile in the p^- region.

The band bending occurs on a depth scale where the image force potential energy

$$E_{imf} = \frac{q^2}{16\pi\epsilon_s x} \qquad (3)$$

contributes significantly to the shape of the total potential energy of the valence band: $E_v(x) = qV(x) + E_{imf}(x)$.[13] This results in a lowering by $\Delta\phi$ of the full Schottky barrier ϕ_{b0} (Fig. 7, top part, solid line). The size of the Schottky barrier lowering is inversely proportional to the depletion width at zero bias w_0. After 4 days we find that $w_0 = 180$ Å and $\Delta\phi$=0.22 eV. At shorter times $\Delta\phi$ is even larger because the depletion depths are smaller (see Fig. 6). The larger the barrier lowering, the smaller the injection barrier is, and the more leakage current of the diode is possible to observe.

Now that we have ascertained the applicability of our calculations in the infinite time limit, we can also analyze the intermediate stages. The calculated energy band diagrams are presented in Fig. 8. Comparison of the ionizable acceptor density profiles after 3 h and 4 days shows that the p^- layer becomes thicker with time and that the ionizable acceptor density decreases with time. This is reflected in the energy band diagram of Fig. 8 by an increase of the depletion width w_0 and, in addition, by a reduction of the image force barrier lowering. The barrier lowering $\Delta\phi$ decreases from 0.28 eV (after 3 h) to 0.22 eV (after 4 days). This change compares well with the change in the Schottky barrier ϕ_b of Fig. 2. The *full* Schottky barrier height stays essentially constant. Since $\phi_{b0}=\phi_b + \Delta\phi$, and using $\phi_b=1.0$ eV from the $J-V$ data taken after 4 days (Fig. 2), we obtain for $\phi_{b0}=1.22$ eV, which brings the Fermi energy level E_F at 0.62 eV above the valence band. This energy distance is the same as found for doped oligomer thiophene diodes with evaporated In contacts.[8] Notably, the obtained position of the Fermi level corresponds to the position of the first bipolaron band of doped $T_{12}d_4$.[8,16]

We add here that we also observed a similar time-dependent behavior of the eutectic Ga,In contact, as described in this article for highly doped $T_{12}d_4$ films, in a series of experiments on unintentionally doped $T_{12}d_4$ films. For both devices the final built-in voltage is the same and pinning of the Fermi level seems to occur similarly as found for devices with evaporated In contacts.[8]

The value of the quality factor n, which is shown in Fig. 3 as a function of time, can in principle discriminate between the types of current transport mechanisms (thermionic versus field emission) that dominate the current across the barrier of the diode.[17] For pure thermionic emission, n is close to 1 and temperature independent. For field emission processes (e.g., tunnel processes) n is generally larger than 1.[13,17] In our experiment, the depletion width at zero bias voltage increases drastically with increasing contact time in agreement with the observed decrease of n in Fig. 3. Therefore, we expect the dominant current transport mechanism across the barrier to change from tunnelling (thin barrier and $n\gg1$) toward thermionic emission (thick barrier and $n\approx1$) (Fig. 3). Note that this interpretation is analogous to that usually proposed for temperature induced changes in n in chemically stable devices.[17] Here n increases with decreasing temperature where the thermionic emission process is inhibited and the current transport is forced to tunnel through the barrier by field emission.

The time-dependent behavior, as observed for eutectic Ga,In contacts, is not observed for evaporated In contacts.

J. Appl. Phys., Vol. 81, No. 8, 15 April 1997

Lous *et al.*   3541

The Ga,In diode seems to slowly approach the stable situation that is directly obtained for evaporated In diodes. For the In diodes a similar built-in voltage of 0.5–0.6 V is found, and the Fermi level seems to be pinned, i.e., independent of the p-dopant concentration. This suggests that during the In-evaporation process a similar chemical reaction between the Schottky metal and the thiophene oligomer occurs, as is found for the Ga,In-droplet deposition at room temperature. In that case, all the time-dependent processes, as observed for Ga,In diodes, are completed faster, in the time span of the In evaporation, because of the elevated temperature of In in the vapor phase. The lower reaction temperature in Ga,In diodes does, however, not stop the chemical reaction, but slows it considerably down. We have also found that in Ga,In diodes the formation of rectifying behavior can be sped up, with about a factor 10, by lowering the pH of the solutions used during the device fabrication. Furthermore, the formation of a lower reverse current density and hence an improved rectification can be accelerated by applying a reverse bias stress, and can be retarded by applying a forward bias stress. For a good understanding of these stress effects, a detailed insight of the reaction mechanism between the Schottky metal and the doped thiophene oligomer is needed.

One way to investigate the chemical nature of the metal–oligomer interface is to analyse a clean Ga,In-incubated surface of a doped thiophene oligomer film with x-ray photoelectron spectroscopy (XPS) as a function of depth (resolution 60 Å) and to compare it with the results of a nonincubated surface. Preliminary measurements, performed in this way, showed that the dopant is uniformly present over the thickness of the film. However, mainly Ga diffuses into the film, where its $2p_{2/3}$ XPS peak obtains a shoulder at the high binding energy side. This means that part of the Ga atoms are present in a bounded phase, for instance, in a similar manner as suggested by Dannetun *et al.* for Al, bounded to the thiophene oligomer.[10] They suggested that the metal, Al in their case, can bind to the thiophene oligomer, such that the conjugation on that specific oligomer molecule is disrupted. A consequence of their model is that this specific oligomer molecule becomes insulating so that the doping reaction is locally inhibited. If this occurs to a fraction of the molecules in the p^- layer, the layer as a whole remains semiconducting, be it with a lower number of acceptors. Electrically, this is observable as a partial undoping of the metal-penetrated p^- layer.

CONCLUSIONS

In conclusion, well-rectifying Schottky diodes are made on highly doped thiophene thin films, using the eutectic Ga, In alloy as the Schottky metal contact. Our studies show that an interaction between the in-diffusing metal and the oligo-

mer occurs, which causes an effective (partial) undoping of the highly doped semiconductor at the Schottky metal interface (formation of a p^- layer on a bulk semiconductor p^+ layer). The decrease of the number of ionizable acceptors at the surface is correlated with the contact time and is probably due to the in diffusion of the Schottky metals and the ongoing chemical reaction between the Schottky metal and the film. Simultaneously with the undoping an eventually well-rectifying barrier on the p^- layer is formed. The full Schottky barrier height stays constant with time. Due to the thin p^- layer present at short contact times, considerable barrier lowering and tunnel processes cause a high reverse leakage current through the diode within the first hours of contact between the Schottky metal and the film. When the p^- layer becomes thicker and progressively less conductive, these leakage currents diminish and the rectification increases.

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