

Schottky barrier induced injecting contact on wide band gap semiconductors

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A new method is proposed by which a minority carrier injecting contact or ohmic contact can be attained in wide band gap II–VI semiconductors. The basic principle is to use a forming process, i.e., an applied electric field at an elevated temperature in the Schottky contact, to spatially separate dopants from compensating centers. In this way, the ratio of dopants to compensating centers can be greatly increased at the semiconductor surface. Upon cooling, the dopant concentrations are frozen to retain a large net concentration of dopants in a thin surface layer, resulting in a depletion layer that is sufficiently thin to allow tunneling injection. Calculations of band profiles, distributions of doping concentrations, and current–voltage characteristics are performed on Al doped ZnTe, in which Al donors complex with doubly negatively ionized Zn vacancies to produce total compensation. The results indicate that the doping concentration and the total band bending during the forming process are the crucial factors for achieving injecting contacts. For Schottky barrier heights above 1 eV, doping concentrations as high as 10^{20} cm^{-3} are needed.

I. INTRODUCTION

A major problem for the wider band gap II–VI compounds has been the inability of conventional processing to dope them both *n* type and *p* type, where selective doping is almost always compensated by opposing charges, arising from defects, impurities, or more complex entities.¹ In recent years, however, new processing methods have overcome this problem in several cases, most notably producing *p* ZnSe.^{2,3} Now a second and more important problem of making good ohmic contact to these materials has become apparent. This is not surprising when one considers that the relevant Schottky barrier heights ϕ_B between these semiconductors and metals such as Au are well over 1 eV. For example, one expects $\phi_B = 1.35 \text{ eV}$ for Au/*n* ZnTe and $\phi_B = 1.28 \text{ eV}$ for Au/*p* ZnSe.⁴ On the other hand, good contacts appear to have been made to ZnTe when the latter is very heavily doped with Al.^{5,6}

The problem in making ohmic contacts to wide band gap materials can be understood very simply in terms of the standard model of the ohmic contact.⁷ An ohmic contact is produced by defeating the Schottky barrier typically existing between a metal and a semiconductor. This is done by doping the barrier region sufficiently heavily to produce a very short depletion region that allows tunneling. For barrier heights as high as the ones found for wide band gap II–VI compounds, the doping concentration necessary is typically well above 10^{19} cm^{-3} . In general, this level of doping is not easily obtained. Doping levels this high have not been reported for bulk *n* ZnTe and *p* ZnSe. For example, observed doping levels for *p* ZnSe saturate at roughly 10^{18} cm^{-3} . The metastable nature of these successful doping schemes makes the possibility of obtaining much higher levels somewhat in doubt.

In this article, we propose a new and very novel way of obtaining high doping levels in the contact region. Under

ideal circumstances, this method could produce highly doped regions in the contact area and lead to ohmic or injecting contacts.

II. PROPOSAL

The method consists of forming the device structure in an electric field at elevated temperatures, to spatially separate the ionized dopants from the compensating centers. Similar ion drift techniques have been applied successfully to other semiconductor device fabrications. For instance, in making *p-i-n* diodes doped with lithium,^{8,9} the mobile interstitial Li with positive charge drifts in the built-in field of the *p-n* junction from the Li⁺-rich *n* side to the Li⁺-deficient *p* side, resulting in the formation of an intrinsic region in between. The drift is usually enhanced by adding a reverse bias to the built-in field. Another example is the measurement of dissociation kinetics of neutral acceptor-hydrogen complexes and donor-hydrogen complexes in hydrogen passivated Si samples by the forming technique.^{10,11} In this technique, the dopant-hydrogen pairs are thermally dissociated, and the charged hydrogens subsequently drift away from the high field depletion region of the reversed biased Schottky diode near the surface.

The basic idea we use here is very simple, as illustrated in Fig. 1. In Fig. 1, we have illustrated the model for the case of Al doped ZnTe, where the Al on a Zn site would be a donor. However, it is thought that an Al donor in ZnTe is usually complexed by a native doubly negative ionized Zn vacancy to form an "A center", which acts as an acceptor to produce the total compensation.^{12,13} This situation is illustrated in Fig. 1(a).

The forming process consists of heating the device structure to a temperature where one of the centers is mobile. Whether the actual mobile species is the V_{Zn}^{-2} or the singly ionized A center is not clear. This might depend on

ZnTe Doped With Al Compensated by Zn Vacancies

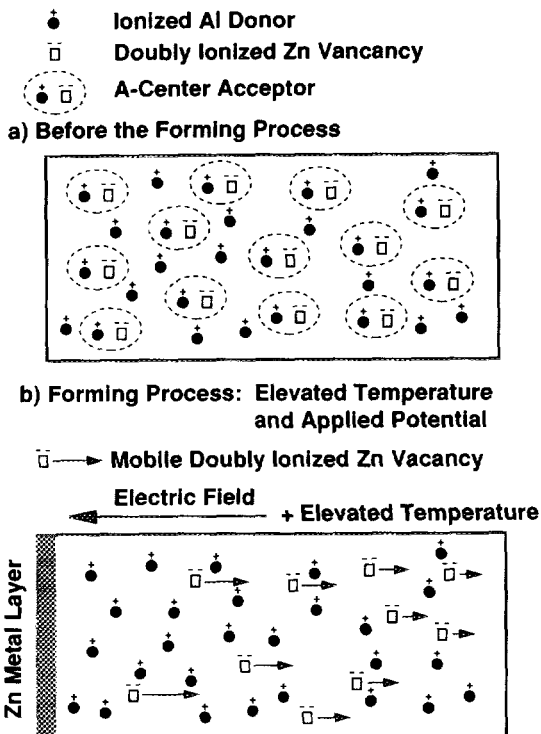


FIG. 1. Schematic of the forming process. The figure illustrates the case of doping of ZnTe by Al. The Al donor is usually complexed by a native doubly negative ionized Zn vacancy V_{Zn}^{-2} to form an A center, which acts as an acceptor. The unformed sample is shown in the upper panel labeled a. The forming process is illustrated in the lower panel labeled b. The Zn vacancies are assumed to be the mobile species which are shown to be moving at the elevated temperature under the influence of the electric field in the semiconductor produced by the Schottky barrier and perhaps an additional applied potential.

many factors, such as the dissociation energy of the A center, the temperature and the strength of the electric field, etc. However, we will see that the key results based on our model are insensitive to this nature of the mobile species. For the example illustrated here, we have selected the V_{Zn}^{-2} as the mobile species, as shown in Fig. 1(b). The presence of an electric field at this elevated temperature will result in the motion of Zn vacancies inside the crystal. We assume that no additional Zn vacancies enter the crystal from the Zn contact. As noted, the charged vacancies move in the electric field in such a way as to produce a highly doped depletion region as shown in Fig. 2. That is, if one of the dopant centers is mobile at the elevated temperature, then the field produced by the Schottky barrier and perhaps an additional applied potential produces a highly doped region with a very narrow depletion width. This depletion region, if thin enough, can result in substantial injection current or an "ohmic contact" to the previously highly self-compensated material.

III. CALCULATIONS

Most of the important parameters governing the calculations are given in Fig. 2. The important energy parameters are the Schottky barrier height ϕ_B , the Fermi energy in

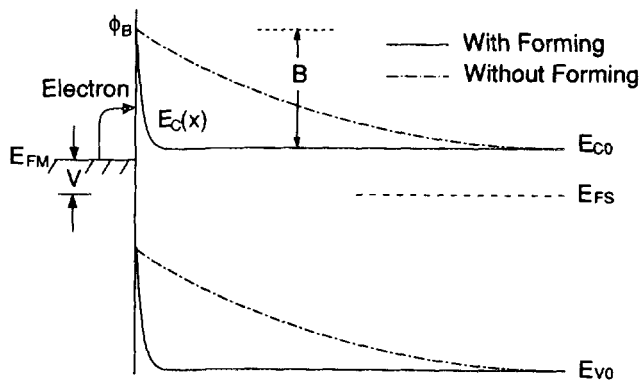


FIG. 2. The energy diagram of the metal-semiconductor interface before and after the forming process. Before the forming process, the nearly perfect self-compensation results in a very lightly doped bulk where the depletion layer is very thick. After the forming process, the self-compensation is not as effective resulting in a very heavily doped region near the surface and a very thin depletion layer.

the metal E_{FM} , the Fermi energy in the semiconductor E_{FS} , which depends on the net doping in the semiconductor, the applied potential V , and the location of the conduction band edge in the bulk semiconductor where the bands are flat E_{C0} . The driving term for the forming process is

$$B = \phi_B - E_{C0} \tag{1}$$

the total band bending across the semiconductor layer. The semiconductor is taken to be nearly fully self-compensated, but with a small net carrier concentration of n_e .

The calculation of the charge rearrangement during the forming process assumes that mobile centers can move and establish thermal equilibrium at the elevated temperatures. The calculations are similar to those reported in Ref. 14. The density of the nonmobile charge centers is assumed to be capped at the original level N_D throughout the process. The final density of mobile centers is taken to be given by

$$N_V = N_S \exp\left(\frac{-2q[E_C(x) - E_{C0}]}{k_B T_f}\right), \tag{2}$$

where N_V is the density of doubly ionized Zn vacancy, N_S is the density of V_{Zn}^{-2} away from the interface, $E_C(x)$ is the conduction band edge as a function of position in the semiconductor, and T_f is the forming temperature. The band profile $E_C(x)$ and the mobile dopant distribution at forming are obtained by solving Poisson's equation

$$\frac{d^2 E_C(x)}{dx^2} = \frac{q}{\epsilon_0 \epsilon} (N_D - 2N_V + p - n), \tag{3}$$

where ϵ is the dielectric constant, n and p are the electron and hole concentrations, respectively.

We assume that the equilibrium distribution of V_{Zn}^{-2} at forming conditions is fixed after cooling to the operating temperature T_m , typically room temperature. Poisson's equation is then solved again to produce the barrier shape with the nonuniform dopant concentration. The current-voltage characteristics at the operating temperature are calculated using a model that includes thermionic emission

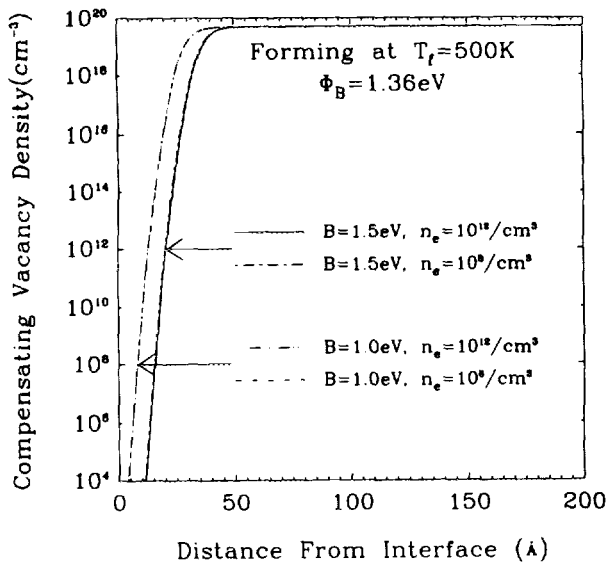


FIG. 3. The computed density of vacancies as a function of distance from the metal–semiconductor interface. The curves are parameterized by the electron density far into the bulk of the material n_e and the total band bending B . The forming temperature is taken to be 500 K and the Schottky barrier height to be 1.36 eV.

over the barrier, field induced emission through the barrier as well as straight tunneling.⁷ The basic equation in this model is

$$J = \frac{qm_c k_B T_m}{2\pi^2 \hbar^3} \int_{E_{CO}}^{\infty} dE T(E) \times \ln \left(\frac{\exp[-(E - E_{FM})/k_B T_m] + 1}{\exp[-(E - E_{FS})/k_B T_m] + 1} \right), \quad (4)$$

where $T(E)$ is the transmission coefficient calculated for the barrier shape given in Fig. 2 using the Wentzel–Kramers–Brillouin (WKB) approximation and two-band $k \cdot p$ model. The applied bias is $V = E_{FM} - E_{FS}$.

IV. RESULTS AND DISCUSSIONS

The results of these calculations are shown in Figs. 3–5. In Fig. 3, we present the compensating vacancy distribution for an Al doping concentration of $N_D = 10^{20} \text{ cm}^{-3}$. The calculations have been performed for the four different combinations of the parameters B ($= 1.5, 1.0 \text{ eV}$) and n_e ($= 10^{12}, 10^8 \text{ cm}^{-3}$). Figure 3 illustrates a number of important points. First, the mobile V_{Zn}^{-2} distributions depend only on the value of B and not the bulk doping value. However, it should be noted that the applied voltage required to maintain the same value of B depends on the background doping in the bulk through the variation of the E_{FS} with doping. Second, the vacancy distribution dips to a very low level for both values of B . This low concentration of vacancies basically exposes all of the dopant atoms, leading to large concentrations of ionized donors.

As expected, these ionized donors make a substantial change in the current–voltage characteristic of the resulting device structure at room temperature. The current–

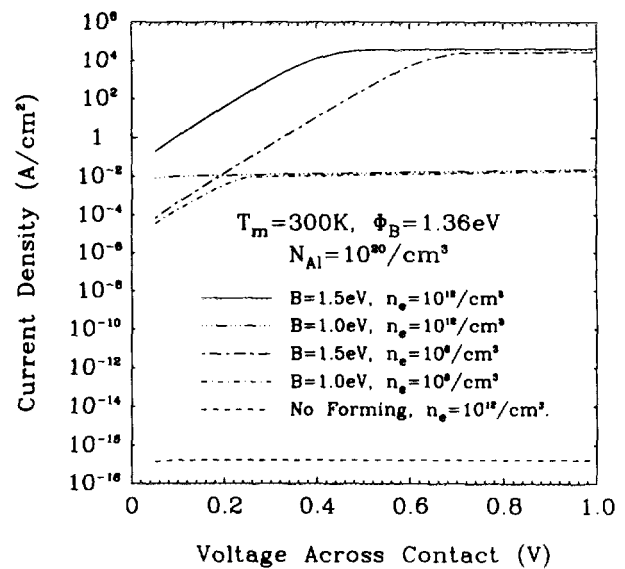


FIG. 4. The current density as a function of applied bias for the unformed and formed devices at 300 K operating temperature. The concentration of Al is taken to be 10^{20} cm^{-3} . The current–voltage characteristic is parameterized by the total band bending potential in the semiconductor during the forming B and the background net doping level in the bulk n_e .

voltage characteristic is shown in Fig. 4 for the case of an Al concentration of 10^{20} cm^{-3} and a V_{Zn}^{-2} concentration of $5 \times 10^{19} \text{ cm}^{-3}$. In Fig. 4, we have a number of different current–voltage characteristics. The lowest current is obtained before the forming. Four different cases are shown after the forming process, B ($= 1.5, 1.0 \text{ eV}$) and n_e ($= 10^{12}, 10^8 \text{ cm}^{-3}$). As can be seen from Fig. 4, the current densities have been greatly enhanced. The largest values of the current are obtained for the highest values of B and background doping n_e . For light emitting diodes, current densities in excess of roughly 10 A/cm^2 are required at relatively small voltage drops, typically less than 1 V. For lasers, 100 A/cm^2 are required at less than 1 V. As can be seen from Fig. 4, only a few cases of doping and forming potential satisfy this criteria.

Since heavy doping of most of these systems is quite difficult, one might ask what effect reducing the doping concentration will have on these results. In Fig. 5, we have plotted the results for an Al dopant concentration of 10^{19} cm^{-3} and a background concentration of V_{Zn}^{-2} of $5 \times 10^{18} \text{ cm}^{-3}$. As can be seen from these results, the currents under similar circumstances of background doping and bias during forming are substantially reduced. In fact, the current densities for all of the voltages of interest are sufficiently small that the contact would not be useful for light emitting devices. The large decrease in current densities is due to the increase in the depletion layer width in going from an Al concentration of 10^{20} cm^{-3} – 10^{19} cm^{-3} .

In our calculation, we have assumed that the mobile centers are doubly ionized under the forming treatment, for which we included the factor of 2 in Eqs. (2) and (3). Since the details of the mobile species are not clear, it is important to see the effect of assuming that the mobile species is instead the singly ionized A center in the case

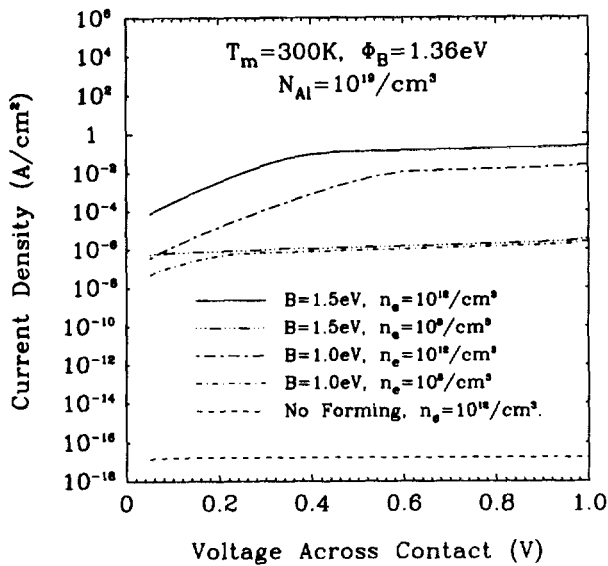


FIG. 5. The current density as a function of applied bias for the unformed and formed devices at 300 K operating temperature. The concentration of Al is taken to be 10^{19} cm^{-3} . The current-voltage characteristic is parameterized by the total band bending potential in the semiconductor during the forming B and the background net doping level in the bulk n_e .

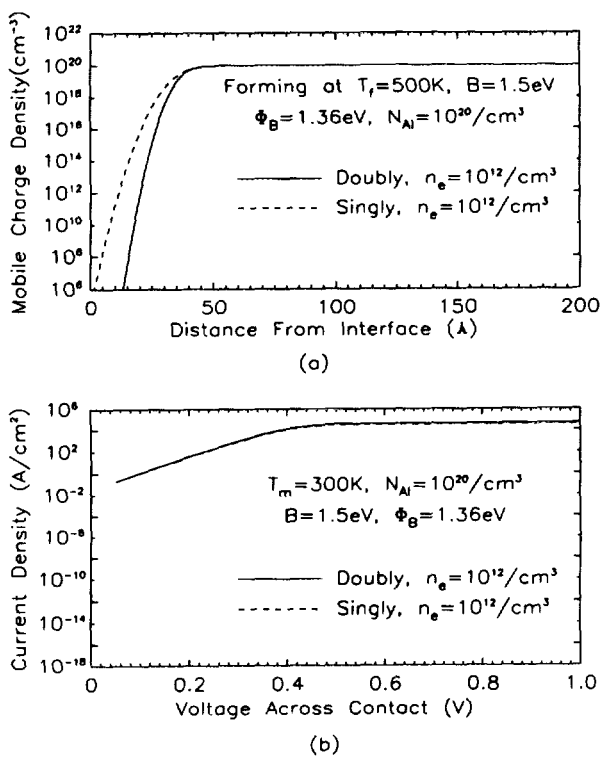


FIG. 6. Comparisons of doubly and singly ionized mobile charge density distributions (a), and the corresponding current-voltage characteristics (b). The mobile charge density distributions shows the difference near the surface. However, the depletion widths are approximately the same, which results in almost identical I - V characteristics.

when the bonding between the V_{Zn}^{-2} and the Al donor is strong. Figure 6 shows the comparisons of doubly and singly ionized compensating mobile charge distributions and the corresponding current-voltage characteristics. The results indicate that although the charge distributions near the surface depend on the mobile charge, the depletion widths are insensitive to the assumption, thus resulting in approximately the same band profile near the contact surface which gives rise to almost identical current-voltage characteristics. Therefore, the results based on our model are independent of the charge of the mobile centers, as long as there exists a mobile charged species which can move and reach thermal equilibrium in the forming process. Preliminary experiments have been performed to support that such forming effects do occur in ZnTe doped with Al.¹⁵

V. CONCLUSIONS

In summary, we have proposed a novel method of obtaining a heavily doped layer for the wide band gap semiconductors in which heavy doping is self-compensated. Using a forming process (elevated temperatures and applied electric field), a mobile species such as a Zn vacancy can be separated from a donor such as Al, leaving behind a high density of uncompensated donors. These donors can substantially change the current-voltage characteristics for Schottky barriers, resulting in an ohmic or an injecting contact. The crucial factors in the forming process for achieving injecting contacts are the doping concentration and the total band bending during the forming process. For Schottky barrier heights above 1 eV, doping concentrations as high as 10^{20} cm^{-3} are needed.

While the specific model and the calculations are presented for the case of ZnTe in which the donor is taken to be Al and the self-compensation mechanism consists of the pairing of two Al donors with the double acceptor produced by a Zn vacancy, one might envision the extension of this approach to produce injecting contacts or ohmic contacts to p ZnSe. While in principle this method could work, the current doping schemes, doping with Li on a Zn sublattice or N on a Se sublattice, involve as yet unexplained self-compensation mechanisms. Basically, what is found is that increasing the Li or N concentrations does not lead to increased doping beyond roughly 10^{18} cm^{-3} . The saturation of doping levels may be due to the formation of electrically inert Li chalcogenides, which are very stable, or N pairs which are bound together by one of the strongest covalent bonds (roughly 9 eV). Hence, it may in fact be difficult to employ such a technique on p ZnSe.

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