Fermi-level-pinning-induced impurity redistribution in semiconductors during epitaxial growth

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The influence of Fermi-level pinning at a semiconductor surface on dopant distribution is demonstrated. It is shown that surface-induced Fermi-level-pinning results in impurity drift during crystal growth by molecular-beam epitaxy. The surface electric field can be screened and reversed by appropriate background doping. Secondary-ion mass spectroscopy measurements indicate a drastic decrease of Si surface drift in $Al_xGa_{1-x}As$ upon screening of the dipole interaction. Reversal of the surface electric field results in a migration of Be impurities in GaAs away from the surface toward the substrate during epitaxial growth.

The miniaturization of semiconductor structures is an important direction in semiconductor physics. As a major consequence of the miniaturization, quantum mechanics became a share of modern semiconductor physics. The scaling down of doping profiles raises the question of the fundamental limits which govern dopant distributions and the physical mechanisms which broaden doping distributions. A well-known mechanism causing redistribution of impurities is *diffusion,* which is the random Brownian motion of impurities in the lattice of a host semiconductor. In this article we show the relevance of a novel mechanism which causes impurities to redistribute and surface segregate, i.e., preferentially migrate toward the growing crystal surface. The segregation is caused by Bardeen's surface states located at an epitaxial crystal surface. The surface states result in the pinning of the Fermi level at the surface and an electronic dipole consisting of electrons localized in surface states and positive donor ions close to the semiconductor surface. Drift of the dopant ions in the dipole field results in dopant redistribution predominantly toward the semiconductor surface. It is further shown that the interaction between surface states and impurities can be screened and reversed by background doping.

Fermi-level pinning at an interface of a semiconductor and a second medium, such as a metal, insulator, or vacuum, is a classic phenomenon in semiconductor physics. The Fermi level at the interface is pinned at an energy $e\phi_B$ below the bottom of the conduction band. Bardeen[1] attributed Fermi-level pinning to interface states which are of donor and acceptor type. Energetically, such Bardeen states can be in the conduction or valence band (e.g., for InAs); more frequently, the states are located close to the middle of the fundamental gap (e.g., GaAs). In an earlier model, Schottky[2] and Mott[3] proposed that the energy $e\phi_B$ of a metal-semiconductor contact equals the difference of the work function of the metal and the electron affinity of the semiconductor. The physical origin of Bardeen's interface or surface states was ascribed to metal-induced gap states[4] or localized states at the semiconductor surface or interface. Such localized states could be due to atomic steps of the surface,[5] defects,[6] or surface reconstruction.[7] Different pinning energies were found for different crystal orientations, e.g., the $\langle 100 \rangle$ and $\langle 110 \rangle$ GaAs orientations.[8] Using angle-resolved photoemission of GaAs(100) surfaces, Chiang *et al.*[7] showed that the Fermi level is pinned at 0.55 ± 0.1 eV above the valence-band maximum for all reconstructed surfaces studied by the group. They proposed that defect states associated with slight nonstoichiometry pin the Fermi level. Fermi-level pinning was found to be insensitive to temperature in the entire temperature range $20° \leq T \leq 500\,°C$,[9] consistent with the fact that the thermal energy kT is much smaller than other relevant energies. Direct-gap $Al_xGa_{1-x}As$ ($x < 0.4$) is known to have a band structure very similar to that of GaAs.[10] Furthermore, properties related to Fermi-level pinning, such as Schottky-barrier height and surface depletion, are known to be very similar for GaAs and direct-gap $Al_xGa_{1-x}As$.[10] Therefore, even though less data are available for $Al_xGa_{1-x}As$, we assume that the Fermi level is pinned during crystal growth of GaAs and $Al_xGa_{1-x}As$ and we will focus on the consequences of such pinning.

To date, the well-known physical *consequences* of Fermi-level pinning are (i) the rectifying characteristics of metal-semiconductor contacts[11,12] and (ii) the depletion of semiconductor surfaces from free carriers.[11] In this study we demonstrate a further consequence of Fermi-level pinning, namely the modification of dopant distribution during crystal growth.

$Al_xGa_{1-x}As$ and GaAs epitaxial layers were grown by molecular-beam epitaxy in a Varian Gen II system at the three substrate temperatures 500, 580, and 660 °C. The layer sequence consists of a 0.3-μm-thick GaAs buffer layer to provide an atomically smooth growth surface followed by 1000 Å of $Al_xGa_{1-x}As$. A δ-function-like doping profile of Si with a concentration $N_{Si}^{2D} = (2-4) \times 10^{12}$

cm^{-2} is obtained by growth interruption followed by a final 1000-Å-thick $Al_xGa_{1-x}As$ layer (2D denotes two dimensional). In a second set of samples with the same geometrical dimensions, Be segregation in GaAs was investigated. Secondary-ion mass spectroscopy (SIMS) measurements are carried out on a PHI 6000 and an Atomica SIMS instrument with Cs^+- and O_2^+-ion sputtering and an acceleration potential of 3 kV.

Si-dopant profiles obtained from SIMS are shown in Fig. 1 for the three samples grown at 500, 580, and 660°C. At a low growth temperature a sharp peak is observed, in agreement with earlier results.[13] The slight asymmetric shape of the SIMS profile obtained at low growth temperature is due to the well-known "knock-on" effect. As the growth temperature is increased, the profiles exhibit significant asymmetry. Surface segregation of dopants is evident from the profiles, especially at $T_s = 660$ °C. The steepnesses of the leading and the trailing slopes of the SIMS spectrum are evaluated in terms of the length in which the Si signal decreases by 1 order of magnitude. The leading slope increases from 35 Å/decade to 390 Å/decade, indicating the drift of impurities toward the surface. The trailing slope increases from 80 Å/decade to 140 Å/decade and indicates diffusion of dopants, which is expected to be symmetric with respect to both sides of the doping spike.

We observe qualitatively the same, but quantitatively weaker, redistribution of impurities toward the surface for Si in GaAs. The smaller redistribution of impurities in GaAs is consistent with the smaller diffusion coefficient found in GaAs as compared to $Al_xGa_{1-x}As$ [see Eq. (5) and Ref. 14]. For the sake of clarity, we show only the data obtained on Si-doped $Al_xGa_{1-x}As$.

Fermi-level pinning at the semiconductor surface causes the doped layer to be depleted of free carriers and a localization of electrons in surface states. If the resulting dipole field is the driving force toward surface segregation, then this segregation process can be reduced by screening the dipole field. Figure 2 shows two SIMS profiles in which p-type Be background doping is included. The concentration of Be is chosen to be $N_A = 4 \times 10^{18}$ cm^{-3} in order to compensate for the Si dopants within 50 Å. Figure 2 reveals that the segregation length is drastically reduced from 150 Å/decade to 80 Å/decade at a growth temperature of 580 °C. The decrease of the segregation length is attributed to the screening of the surface dipole caused by Fermi-level pinning. The trailing slope of the SIMS profile is changed insignificantly, indicating that diffusion and the "knock-on" effect are not influenced by background doping. The SIMS profile for the sample grown at $T = 660$ °C shows the same qualitative trend as the sample grown at the intermediate temperature (see Figs. 1 and 2). The surface-segregation length is reduced and the SIMS profile has a more symmetric shape, indicating that diffusion dominates the dopant redistribution. The results show that the electronic property of Fermi-level pinning causes significant (structural) redistribution of dopants during growth and that this interaction can be screened by appropriate background doping.

A net shift of the entire Si peak towards the surface with higher growth temperature is found experimentally, as shown in Figs. 1 and 2. While the net shift is expected without background doping (Fig. 1), it is unexpected with background doping (Fig. 2). We therefore attribute the shallower depth of the Si peak at high growth temperatures to a thinner $Al_xGa_{1-x}As$ top layer. At the high

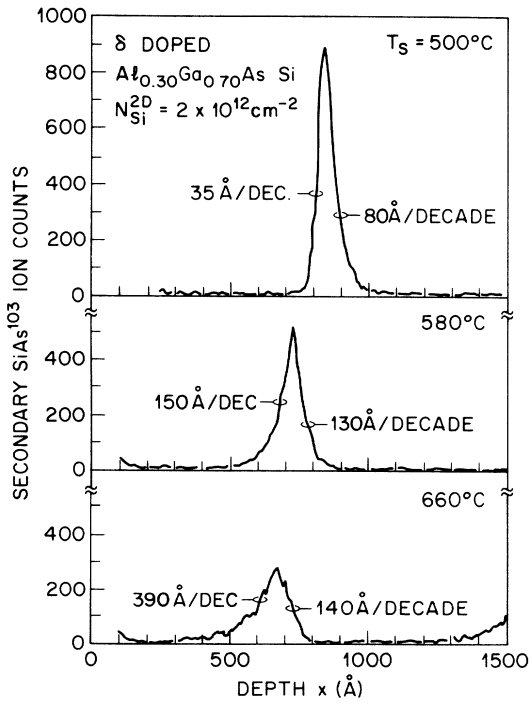

FIG. 1. Secondary-ion mass spectroscopy profile of Si in epitaxial $Al_{0.30}Ga_{0.70}As$ for three different samples grown at 500, 580, and 660 °C by molecular-beam epitaxy. The Si is deposited during growth interruption to achieve a δ-function-like doping profile.

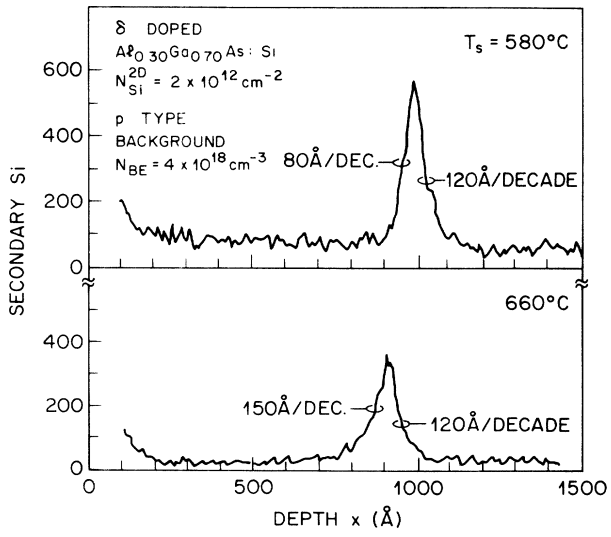

FIG. 2. Secondary-ion mass spectroscopy profile of Si in $Al_{0.30}Ga_{0.70}As$ grown at 580 and 660 °C. The entire epitaxial layer is homogeneously doped with Be.

growth temperature of 660 °C, reevaporation of $Al_xGa_{1-x}As$ is known to occur, which results in a smaller thickness of the top $Al_xGa_{1-x}As$ cap layer.

The observed effect is even more striking for Be surface segregation in GaAs, as shown in Figs. 3(a)–3(c). At low growth temperatures [see Fig. 3(a)], the shape of the SIMS profile is dominated by the "knock-on" effect. At elevated growth temperatures [see Fig. 3(c)], surface segregation of Be becomes evident. The Be profile for Si-background doping is shown in Fig. 3(d). The most striking feature is that the Be profile is strongly skewed towards the substrate side: Owing to reversal of the surface electric field, Be impurities are driven away from the surface in the direction of the substrate. The very asymmetric shape of the Be profile of Fig. 3(d) cannot be explained by the "knock-on" effect.

Traditional theories of surface segregation are based on the concept that a lower surface energy and a higher volatility of dopants are driving forces toward surface segregation. The reduction of the total energy can be, for example, a reduction of strain energy. In the model discussed here, the reduction in total energy is mediated by the reduction of the *electronic part* of the energy. The driving force, i.e., a lower surface energy, is therefore identical for traditional theories on surface segregation and the Fermi-level-pinning–induced drift model. The terms Fermi-level-pinning–induced *segregation* and Fermi-level-pinning–induced *drift* are therefore equivalently well suited for the effect of the redistribution of impurities. Overbury *et al.*[15] calculated segregation in

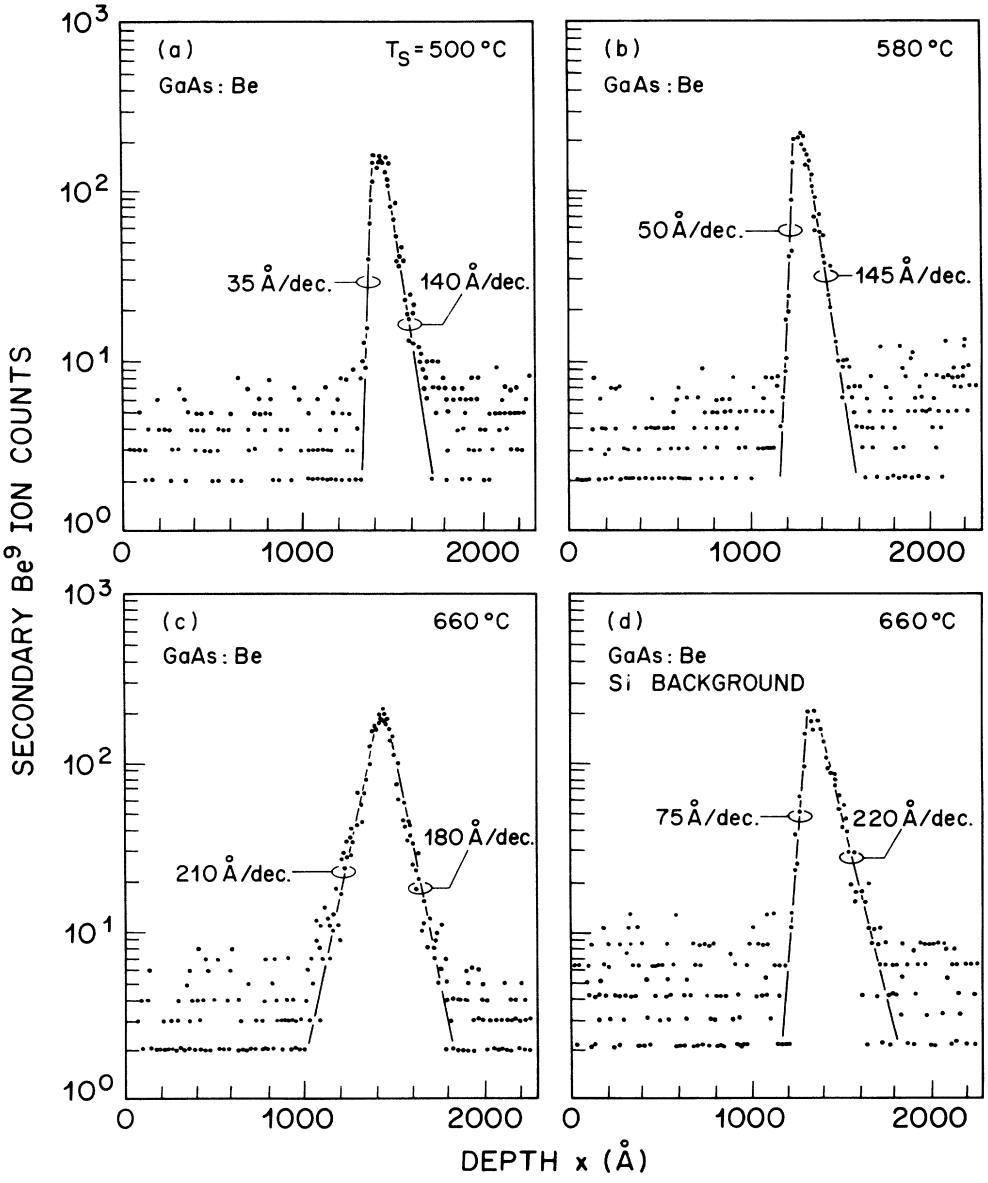

FIG. 3. Secondary-ion mass spectroscopy profile of Be in epitaxial GaAs grown at (a) 500 °C, (b) 580 °C, and (c) 660 °C. Inclusion of Si-background doping at a growth temperature of 660 °C results in migration of Be toward the substrate during growth.

binary systems based on chemical thermodynamics. Their result does not suggest Si segregation in GaAs. Furthermore, Beall *et al.*[16] state that Si segregation in GaAs driven by a lower Si-surface energy is not likely. Panish[17] showed that Sn incorporation in GaAs grown by liquid-phase epitaxy is controlled by equilibrium between the liquid and the crystal surface and influenced by the Fermi level at the growing surface.

Next, we will quantitatively analyze the surface-segregation process and show that the experimental data are in agreement with theory. We will first neglect any diffusion effects and consider only segregation. The band diagram of a semiconductor containing a δ-function-like doping profile is shown in Fig. 4(a). Figure 4(b) shows that inclusion of appropriate background doping results in *reversal of the surface electric field,* which represents a driving force for impurities toward the substrate.

The surface of the semiconductor is assumed to be moving along the x direction with a velocity v_s. For a two-dimensional doping density of N_D^{2D}, the electric field of the dipole is given by

$$\mathbf{E}=\begin{cases} eN_D^{2D}/\epsilon\ , & \text{(1a)} \\ \phi_B/(x_s-x_d)\ , & \text{(1b)} \end{cases}$$

where e is the elementary charge, ϵ is the permittivity, and $x_s=v_s t$ and x_d are the position of the surface and the doped layer, respectively. Equation (1a) is valid if the doped layer is depleted of all free carriers, i.e., $x_s-x_d\le\phi_B\epsilon/eN_D^{2D}$, while Eq. (1b) is valid if the doped layer is partly depleted of free carriers, i.e., $x_s-x_d\ge\phi_B\epsilon/eN_D^{2D}$. The segregation velocity of dopants is given by

$$v_d=\frac{dx_d}{dt}=\mu\mathbf{E} \tag{2}$$

where μ is the doping-ion mobility, which is obtained from the diffusion coefficient of Si in $Al_xGa_{1-x}As$ (Ref. 14) ($D_0=4\times10^{-8}$ cm^2/s, $E_a=1.3$ eV) and the Einstein relation $\mu=De/kT$. Certainly the validity of the Einstein relation is restricted to impurities which are ionized, i.e., which occupy substitutional sites. The good electrical activity of Si impurities in GaAs and $Al_xGa_{1-x}As$ was confirmed previously.[14] Note that Eq. (2) and the Einstein relation apply to any diffusion mechanism, for example, the substitutional mechanism or the substitutional-interstitial mechanism, provided that the initial and final sites of the atomic-diffusion jump are substitutional sites.

For small distances between the doped layer and the surface, the dipole field is given by Eq. (1a) and the segregation velocity of the dopants is given by

$$v_d=\frac{De}{kT}\frac{eN_D^{2D}}{\epsilon}\ . \tag{3}$$

At 500 °C the diffusion coefficient is $D=2.5\times10^{-16}$ cm^2/s and Eq. (3) yields $v_d=0.1$ Å/s for the segregation velocity, which is a small segregation velocity. However, at $T=660$ °C one obtains $D=6\times10^{-15}$ cm^2/s, where the segregation velocity is 2 Å/s, which is comparable in magnitude to the growth velocity (v_g) of 1.29 μm/h = 3.6 Å/s for $Al_{0.30}Ga_{0.70}As$ (0.9 μm/h for GaAs). Thus, significant segregation is expected to occur at $T=660$ °C.

To obtain a single differential equation for small x_s-x_d and large x_s-x_d, the electric field given in Eqs. (1a) and (1b) is approximated by

$$\mathbf{E}=\left[\left[\frac{e}{\epsilon}N_D^{2D}\right]^{-1}+\left[\frac{\phi_B}{x_s-x_d}\right]^{-1}\right]^{-1}\ . \tag{4}$$

which represents a lower limit of the true field in the intermediate range. The differential equation then becomes

$$\frac{dx_d}{dt}=\frac{De}{kT}\left[\frac{\epsilon}{eN_D^{2D}}+\frac{x_s-x_d}{\phi_B}\right]^{-1}\ , \tag{5}$$

with $x_s=v_s t$. We solved this nonlinear differential equation numerically for the three growth temperatures, a (experimental) carrier density of $N_D^{2D}=2\times10^{12}$ cm^{-2}, and a total growth time of $t=280$ s. The results of the numerical solution are as follows: At a low substrate temperature of 500 °C the segregation during growth of the 1000-Å-thick top layer is 12 Å. The corresponding calculated segregation lengths at growth temperatures of 580 and 660 °C are 64 and 293 Å, respectively. These calculated segregation lengths are in good qualitative agreement with the experimental results displayed in Fig. 1.

These approximate calculations allow us to estimate the relative importance of the diffusion and the segregation process. The diffusion length is known to equal ap-

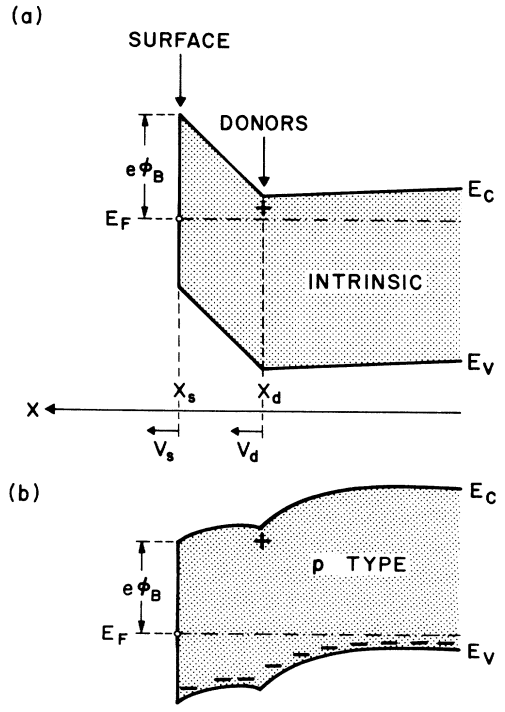

FIG. 4. (a) Band diagram of an n-type semiconductor subject to Fermi-level pinning and a δ-function-like doping profile. (b) Dipole interaction between surface and doped layers can be screened and reduced by p-type background doping.

proximately $\sqrt{Dt}$. According to Eq. (5), the segregation length is proportional to Dt. Since D depends exponentially on temperature, diffusion ($\sqrt{Dt}$) dominates at low temperatures, while segregation (Dt) will dominate at higher temperatures; this trend is clearly confirmed by our experiments.

The calculation above, although it gives a very good explanation of the physical process causing surface segregation, is unrealistic in two respects. First, since diffusion of impurities was neglected, the impurity profile remains δ-function-like. The second insufficiency of the calculation is the omission of screening. At a growth temperature of 660 °C the concentration of thermally excited, intrinsic carriers reaches a value of $n_i \cong 10^{16}$ cm^{-3}, which corresponds to a Debye screening length of ≅550 Å.

The understanding of the segregation mechanism opens up new ways to either make use of the mechanism or to avoid segregation in these semiconductors. The possible uses include the controlled field-driven redistribution of dopants close to the surface. On the other hand, possibilities of reducing the segregation include (i) illumination of the growing surface to increase the carrier density and the screening, (ii) growth on different surface orientations such as the (110) plane on which the Fermi-level pinning is reduced, and (iii) growth at low temperatures.

Our findings of Fermi-level-pinning–induced surface drift also explain observations reported previously: Tejwani *et al.*[18] found that the abruptness of Be-dopant distribution improves uon Si-background doping in GaAs, which can be explained by our model. Beall *et al.*[16] found Si segregation at high concentrations in GaAs. Nichols *et al.*[19] reported high concentrations of impurities close to the surface in GaAs, which can be consistently identified as a result of Fermi-level-pinning–induced segregation.

In conclusion, Fermi-level pinning at semiconductor interfaces has consequences exceeding the well-known Schottky-barrier and surface-depletion effects. The electronic property of Fermi-level pinning results in structural changes in the doping profile of a growing semiconductor in terms of a redistribution of impurities toward the surface: The electrostatic dipole interaction between carriers localized in surface states and their parent donors causes the donor to segregate along with the growing surface. The segregation is reduced by screening, which is experimentally achieved by appropriate background doping. Furthermore, appropriate background doping *reverses* the surface electric field, which results in a drift of dopants toward the substrate, as observed for Be in GaAs.

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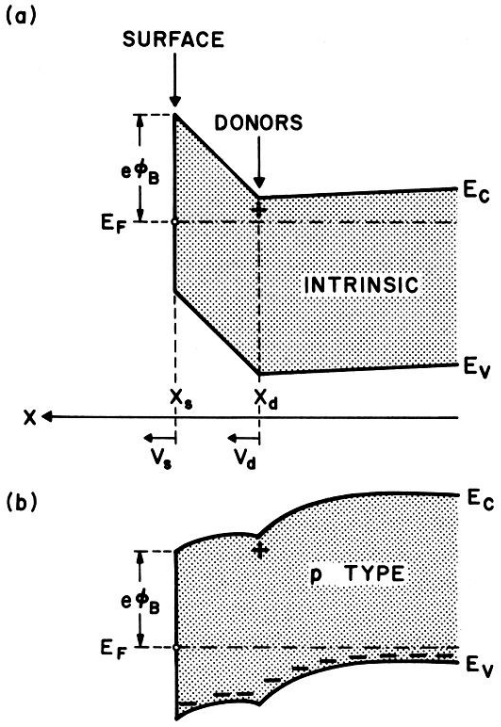

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