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MICROSCOPIC MECHANISM OF GaAs SCHOTTKY BARRIER FORMATION

W. Walukiewicz

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Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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Microscopic mechanism of GaAs Schottky barrier formation

W. Walukiewicz

Center for Advanced Materials, Lawrence Berkeley Laboratory,
University of California, Berkeley, California 94720

ABSTRACT

Thermodynamic properties of native defects in the arsenic rich layer of GaAs at the interface are used to develop a new microscopic model of metal-GaAs Schottky barriers. The model takes into consideration the roles played by the native defects and electronegativity of the metal. It offers a comprehensive explanation of experimental data on Fermi level pinning at the surface as well as on Schottky barrier heights determined from electrical measurements.

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Understanding of the nature of the physical processes leading to formation of Schottky barriers (SB) at a metal-semiconductor interface is one of the central problems of solid state physics.[1,2] Because of its practical importance, the metal-GaAs system is currently being extensively studied. Despite an enormous amount of experimental and theoretical research, there is no generally accepted model to explain the observed properties of GaAs SBs.[2,3] A number of approaches have been proposed which relate metal and/or GaAs properties to SB characteristics. They have been based on the assumption that either native defect states such as As and Ga vacancies,[4,5] or As and Ga antisites[6] pin the Fermi energy at the interface, or that the SB height is determined by an "effective" work function of the reacted metal-semiconductor interface layer.[7] There were also models proposed relating Fermi energy pinning to intrinsic semiconductor band gap states induced by the metal.[8,9,10] Although each of these models have met with some success in explaining some properties of SBs on GaAs, they could not unambiguously identify extrinsic and intrinsic characteristics of metal-semiconductor interfaces which determine barrier heights for a large variety of metals.

In this letter a new model of GaAs-metal SBs is presented. The native defects responsible for the barrier formation are identified and the role of electronegativity of the metal is clarified. A detailed microscopic mechanism of SB formation is proposed which very well accounts for the known experimental data on GaAs SBs, and which predicts new features of the barriers which can be verified experimentally.

It is well established experimentally that excess arsenic is always present on GaAs surfaces and in a thick layer close to the surface independent of the surface preparation technique and type of the bulk

doping.[11,12] The reactions leading to excess arsenic due to oxidation or metalization of GaAs were discussed recently.[7] These findings indicate that close to the interface an arsenic rich (or Ga deficient) layer of GaAs exists. To accommodate this non-stoichiometry certain native defects are formed. It has been shown that there are two dominant native defects which are formed in arsenic rich GaAs: a gallium vacancy V_{Ga} which is an acceptor and a donor complex (As_{Ga},V_{As}).[13,14] Although these defects have very much different electrical properties they are structurally similar, namely, they can be formed one from the other by a simple displacement of an arsenic atom between gallium and arsenic sites. The energy required for such transformation is very small and it can easily occur at room temperature.[15] The property of this defect system, which is essential for the present model, is a strong dependence of the defect reaction $(As_{Ga},V_{As}) \rightleftharpoons V_{Ga}$ on the Fermi energy, E_F, location in the band gap.[13,15,16] Thus, for $E_F < E_v + 0.5$ eV $(As_{Ga},V_{As})^{3+}$ donor in the triply ionized state is the stable defect, whereas for $E_F > E_v + 0.7$, V_{Ga}^{3-} will be formed.[15] In the energy range $E_v + 0.5$ eV $< E_F < E_v + 0.7$ eV both defects can be formed and compensate each other.

In order to construct a model Schottky barrier on GaAs we will assume that there exists a thin layer of thickness D at the GaAs surface which is homogeneously depleted of Ga. It will become clear later that the uniformity of the defect distribution in the layer is not a critical assumption. We consider n- and p-type GaAs doped to the level N_d and N_a, respectively, which is brought into intimate contact with a metal of known internal work function, φ_m^I (or electronegativity X_m).[17] Three different cases, corresponding to distinct ranges of the value of metal work

function, are possible for n-type GaAs: (1) $\varphi_m^I - X_S > E_g - 0.5$ eV; (2) $\varphi_m^I - X_S < E_g - 0.7$ eV; and (3) $E_g - 0.7$ eV $< \varphi_m^I - X_S < E_g - 0.5$ eV, where $E_g = 1.42$ eV is the GaAs band gap and χ_S is the GaAs electron affinity. In the first case [schematically shown in Fig. 1(b)], the Fermi energy at the interface falls below $E_v + 0.5$ eV level, therefore $(As_{Ga}, V_{As})^{3+}$ donors are formed to accommodate excess arsenic. A depletion layer is created. The thickness of the layer d is determined by the (As_{Ga}, V_{As}) donor concentration N_D and by the condition that, at the edge of the depletion layer, the Fermi energy moves above $E_v + 0.5$ eV. As it was discussed above, in such a case (As_{Ga}, V_{As})donors will be partly transformed into V_{Ga} acceptors, and the material will become compensated. The position of the Fermi energy for $d < x < D$ will be controlled by charge balance between deep donors and acceptors and the net concentration of shallow donors (n-type material). For $x > D$ a standard thick depletion layer controlled by the bulk doping N_d is formed with the barrier heights $E_g - 0.7 < \phi_{Bb}^n < E_g - 0.5$.

A different situation occurs for the second case when the Fermi energy at the interface is located above the $E_v + 0.7$ eV level, i.e. $\varphi_m^I - X_S < E_g - 0.7$ eV shown in Fig. 1(c). Such a location of Fermi energy will induce formation of the acceptor defects $(V_{Ga})^{3-}$ and therefore a p-type-like depletion layer of a thickness d will be formed at the interface. As shown in Fig. 1(c), in this range the Fermi energy moves rapidly with respect to the conduction band until it falls below $E_v + 0.7$ eV where again material is becoming compensated. As in the previous case for $x > D$ a barrier ϕ_{Bb}^n, controlled by the bulk doping N_d, is formed. Finally, for the third case $E_g - 0.7$ eV $< \varphi_m^I - \chi_S < E_g - 0.5$ eV, shown in Fig. 1(c), the Fermi energy at the interface is located at the level at

which both the deep donors and acceptors are formed, resulting in a compensated layer of the thickness D. Again, beyond the gallium depleted layer, i.e. for $x > D$, a thick barrier controlled by bulk doping N_d is formed.

A very important result of this analysis is that in all three cases, independent of the value of metal work function, the height of the thick barrier ϕ_{Bb}^{n} is determined by the bulk doping and is in the range 0.72 eV to 0.92 eV. Identical analysis for metal-(p-type GaAs) contacts provide similar results with the thick barrier controlled by bulk doping of concentration N_a. Height of the barrier is in the range of energies 0.5 eV $\leq \phi_{Bb}^{P} <$ 0.7 eV. It is therefore clear that the thin, arsenic rich layer at the GaAs surface can act as a buffer layer accommodating a part of the potential difference $\varphi_m^I - \chi_S$, so that the Fermi level is pinned in a narrow range of energies.

In order to find the final position of the Fermi energy in the compensated layer, we have to examine more carefully the relationship between metal electronegativity and an "effective" electronegativity of GaAs, defined as an ability of GaAs to attract electrons. According to a general rule, metals with the electronegativity larger (smaller) than the "effective" electronegativity of GaAs, X_{GaAs}^{eff}, induce transfer of electrons to (from) the metal from (to) GaAs. The Fermi energy level in the compensated region is determined by a delicate balance between deep donors and deep acceptors. Any external perturbation of the balance will easily result in a shift of Fermi energy within the energy range (E_v + 0.5 eV), (E_v + 0.7 eV). Therefore, metals with $X_m > X_{GaAs}^{eff}$ will induce a downward shift of the Fermi energy by removing electrons from GaAs, and metals with $X_m < X_{GaAs}^{eff}$ will result in a shift of the Fermi energy towards the upper level E_v + 0.7 eV. The final heights of the thick barriers are

$\phi_{Bb}^{n} = 0.92$, $\phi_{Bb}^{p} = 0.5$ eV for the former and $\phi_{Bb}^{n} = 0.72$, $\phi_{Bb}^{p} = 0.7$ eV for the latter case. A special situation occurs when $X_m \simeq X_{GaAs}^{eff}$. Since there is no charge transfer in this case, Fermi energy in the compensated layer will be located at the energy at which defect formation energies for (As_{Ga}, V_{As}) and V_{Ga} are equal. This, according to Ref. 13, occurs for $E_F \sim E_v + 0.6$ eV. Thus for $X_m = X_{GaAs}^{eff}$ the values of the barrier heights are $\phi_B^n \simeq 0.82$ eV and $\phi_B^p = 0.6$ eV, respectively. It will be shown in a forthcoming longer paper that the electron transport through the thin surface barrier ϕ_{Bs}^{n} [see Fig. 1(b)] is controlled by a thermionic-field emission, and that the effective barrier observed in electrical measurements is well-approximated by ϕ_{Bb}^{n}, although the Fermi energy pinning at the surface is given by $\phi_{Bb}^{n} + \phi_{Bs}^{n}$.

The above considerations give a general rule for prediction of SB height for different metals, providing the effective electronegativity of GaAs is known. In Fig. 2 experimental data for SBs for metals with different electronegativities are shown. A very distinct transition from almost equal Schottky barriers $\phi_B^n \simeq \phi_B^p = 0.7$ eV for low electronegativities to $\varphi_B^n \simeq 0.9$ and $\varphi_B^p \simeq 0.5$ for large electronegativities[18] is observed. The transition occurs at about $X_m = 1.8$ eV, where, as is shown for the case of Ni, $\phi_B^n \simeq 0.8$ and $\phi_B^p \simeq 0.6$ eV. This is exactly a behavior predicted by our model, assuming $X_{GaAs}^{eff} = 1.8$ eV. Interestingly enough, this value is equal to an average of electronegativities for Ga(1.6eV) and As(2.0eV)[18]. The lines in Fig. 2 represent theoretical values of barrier heights given by the present model. The experimentally measured barriers are on average slightly lower than the predicted ones. This is, however, understandable as the effects which lower the barrier heights, such as image force, were neglected.

Bearing this in mind it is seen in Fig. 2 that the predictions of the present model agree remarkably well with the experiments. A meaningful exception from the rule is Al, which with X_m = 1.5 eV is predicted to have $\phi_B^n \simeq 0.72$ eV and $\phi_B^p \simeq 0.7$ eV. These values differ substantially from experimentally found $\phi_B^n \simeq 0.8$ eV and $\phi_B^p \simeq 0.6$ eV.[19,3] This could indicate that an epitaxial layer of AlAs or $Al_{1-x}Ga_xAs$ is formed during deposition so that an effective electronegativity of these compounds, rather than Al, determines the barrier height.

In the present model some of the phenomenonological rules found for SBs in GaAs find a straightforward explanation. Accordingly, it is evident that the commonly invoked and experimentally confirmed[3] rule $\phi_B^n + \phi_B^p \simeq E_g$ is justified in the present model. Also, a reported dependence of the ϕ_B^n on electronegativity can be easily deduced from the model which predicts the total SB height change of 0.2 eV. This value together with a range of metal electronegativities 1.2 eV to 2.4 eV gives $\Delta\phi_B/\Delta X_m \simeq 0.17$, which favorably compares with the experimental value of 0.15 listed in Ref. 17.

Excellent confirmation of the present model has been provided in recent experiments on the dependence of the Fermi energy pinning on deposited Au layer thickness observed on n- and p-type GaAs.[21] It has been shown that for submonolayer coverage the Fermi energy shifts with increasing layer thickness towards a level E_v + 0.6 eV in both n- and p-type GaAs. For even thicker Au layers the pinning level shifts downward to about E_v + 0.1 eV. This is precisely a type of behavior predicted by our model. According to the model, deep acceptors V_{Ga} are formed in n-type and deep donors (As_{Ga},V_{As}) are formed in a p-type material close to the surface. Because at these low coverages the metal work function does

not play any role, thus the Fermi energy in the case of sufficiently large defect concentrations will be pinned at the energy at which the balance between the deep donor and deep acceptor concentrations is achieved, i.e. at $\sim E_v + 0.6$ eV.[13] For thicker metal layers the internal work function (or electronegativity) is a well-defined parameter affecting distribution of charge at the interface. Thus, as is seen in Fig. 1, Fermi energy very close to the surface is given by $\phi^n_{Bb} + \phi^n_{Bs} = \varphi^I_m - \chi_S$ for both n-type and p-type GaAs. From the experimental data[21] $\varphi^I_m - \chi_S = 1.3 \pm 0.1$ eV for Au, which with $\chi_S = 4.07$ eV gives the value $\varphi^I_m \approx 5.37 \pm 0.1$ eV. This value is close to the range of experimentally measured work functions 5.1 to 5.3 eV[1] for gold. It should be emphasized here that although the Fermi energy at the surface is pinned at $\sim E_v + 0.1$ eV, the SB heights measured on thick contacts are according to our model, given by the thick bulk barrier and have values $\phi^n_{Bb} = 0.92$ eV and $\phi^p_{Bb} \simeq 0.5$ eV. This, as is seen in Fig. 2, agrees very well with SB heights determined from I-V characteristics. This means that the SB heights determined from the Fermi energy pinning measured using surface spectroscopic techniques may in some instances have very little in common with SB height deduced from I-V characteristics.

A number of possible experiments to verify our model can be envisioned. First, according to the model the Fermi energy position at the surface should depend on the metal work function for thick metal layers. Therefore the measurements similar to those performed in Ref. 21 for metals with different work functions should provide very much different energies at which the Fermi level is pinned. Secondly, as it has been shown recently, metals deposited at lower temperatures do not exhibit charactistic pinning at $E_v + 0.6$, suggesting low concentrations of the native defects created at low temperatures[22]. The present model

predicts that in the absence of these defects there is no thin barrier ϕ_{Bs}^{n} at the surface and thus the barrier height determined from the Fermi energy pinning at the interface has the same value as that found from the electrical measurements and should be equal to $\varphi_{m}^{I} - \chi_{S}$.

The basic component of the present model is an existence of the pair of closely related native defects with very much different electrical properties. Since the properties of SBs on other III-V semiconductors show some similarities to that of GaAs it is tempting to suggest that similar models could be applicable to other semiconducting compounds. However, before it can be done, better understanding of the thermodynamics of native defects as well as more reliable data on properties of SBs on these materials are needed.

In summary, a detailed model of Schottky barrier formation, comprising effects of native defects and metal work function, has been developed. The model explains very well various experimental observations on GaAs-metal contacts.

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REFERENCES

1. E.H. Rhoderick, Metal Semiconductor Contacts (Clarendon Press, Oxford, England 1980).

2. R.H. Williams, in Physics and Chemistry of III-V Compound Semiconductor Interfaces, edited by C.W. Wilmsen (Plenum Press, New York and London, 1985).

3. G.Y. Robinson, in Physics and Chemistry of III-V Compound Semiconductor Interfaces, edited by W. Wilmsen (Plenum Press, New York and London, 1985).

4. W.E. Spicer, I. Lindau, P.R. Skeath, C.Y. Su and P.W. Chye, Phys. Rev. Lett. 44, 429 (1980).

5. W.E. Spicer, I. Lindau, P. Skeath and S.Y. Su, J. Vac. Sci. Tech. 17 1019 (1980).

6. O.F. Sankey, E. Allen, Sheng-Fen Ren and J. Dow, J. Vac. Sci. Technol. B3, 1162 (1985).

7. J.L. Freeouf and J.M. Woodall, Appl. Phys. Lett. 39, 727 (1981).

8. V. Heine, Phys. Rev. A138, 1689 (1965).

9. S.G. Louie and M.L. Cohen, Phys. Rev. B13, 2461 (1976).

10. J. Tersoff, Phys. Rev. Lett. 52, 465 (1984).

11. W. Mönch, Surf. Science 132, 92 (1983).

12. Z. Liliental-Weber, E.R. Weber, N. Newman, W.E. Spicer, R. Gronsky and J. Washburn, Proc. XIV Intern. Conference on Defects in Semiconductors, (Paris, 1986), in press.

13. G.A. Baraff and M. Schlüter, Phys. Rev. B33, 7346 (1986).

14. G.A. Baraff and M. Schlüter, Phys. Rev. Lett. 55, 1327 (1985).

15. Y. Bar-Yam and J.D. Joannopoulos, Phys. Rev. Lett., 56, 1213 (1986). The theoretical values of the native defect energy levels found in this reference and in Refs. 13 and 14 agree surprisingly well with Fermi energy pinning levels required to explain experimental barrier heights at room temperature. This agreement must be considered fortuitous because of limited accuracy of the theoretical calculations. In fact, the characteristic thermodynamic properties of the native defects in GaAs are more important for the present model than the energy level position which can eventually be found comparing predictions of the model with experimental data.

16. G.A. Baraff and M. Schlüter, Phys. Rev. Lett. 56, 1214 (1986).

17. M. Schlüter, Phys. Rev. B17, 3044 (1978). As was discussed in this ref., quantity which is directly related to electronegativity (on a Pauling Scale) is internal work function φ_m^I. In the present paper we use φ_m^I rather than experimentally measured and commonly cited work function φ_m.

18. L. Pauling, The Nature of the Chemical Bonds, (Cornell University Press, Ithaca, NY, 1960).

19. J.R. Waldrop, Appl. Phys. Lett 44, 1002 (1984).

20. N. Newman, M. van Schilfgaarde, T. Kendelewicz, M.D. Williams and W.E. Spicer, Phys. Rev. B33, 1146 (1986).

21. W.G. Petro, I.A. Babalola, P. Skeath, C.Y. Su, I. Hino, I. Lindau and W.E. Spicer, J. Vac. Sci. Technol. 21, 585 (1982).

22. F. Schäffler and G. Abstreiter, J. Vac. Sci. Technol. B3, 1184 (1985).

FIGURE CAPTIONS

Fig. 1 a) Profiles of native defects N_D,N_A and bulk impurity N_d concentrations. b), c), and d) Band diagrams of Schottky contacts for metals with different work functions.

Fig. 2 Schottky barrier height for n-type and p-type GaAs as functions of metal electronegativity. Experimental values are the average of the barrier heights given in Refs. 19,20 and listed in Ref. 3.

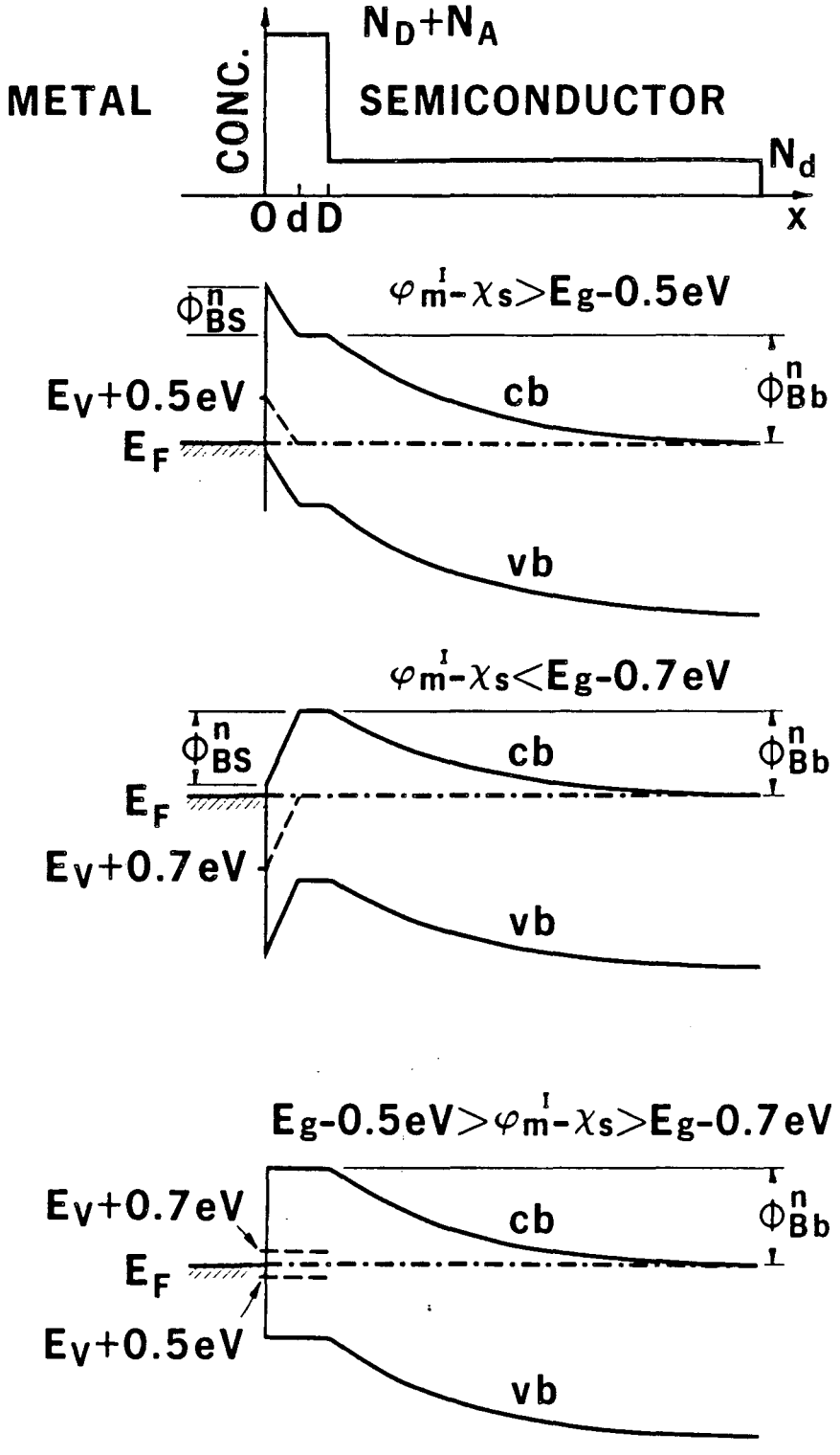
METAL
CONC.
N_D+N_A
SEMICONDUCTOR
N_d
O d D
x
$\varphi_m^I-\chi_s>E_g-0.5eV$
Φ_{BS}^n
$E_V+0.5eV$
cb
Φ_{Bb}^n
E_F
vb
$\varphi_m^I-\chi_s<E_g-0.7eV$
Φ_{BS}^n
cb
Φ_{Bb}^n
E_F
$E_V+0.7eV$
vb
$E_g-0.5eV>\varphi_m^I-\chi_s>E_g-0.7eV$
$E_V+0.7eV$
cb
Φ_{Bb}^n
E_F
$E_V+0.5eV$
vb
XBL 868-3143

Figure 1.

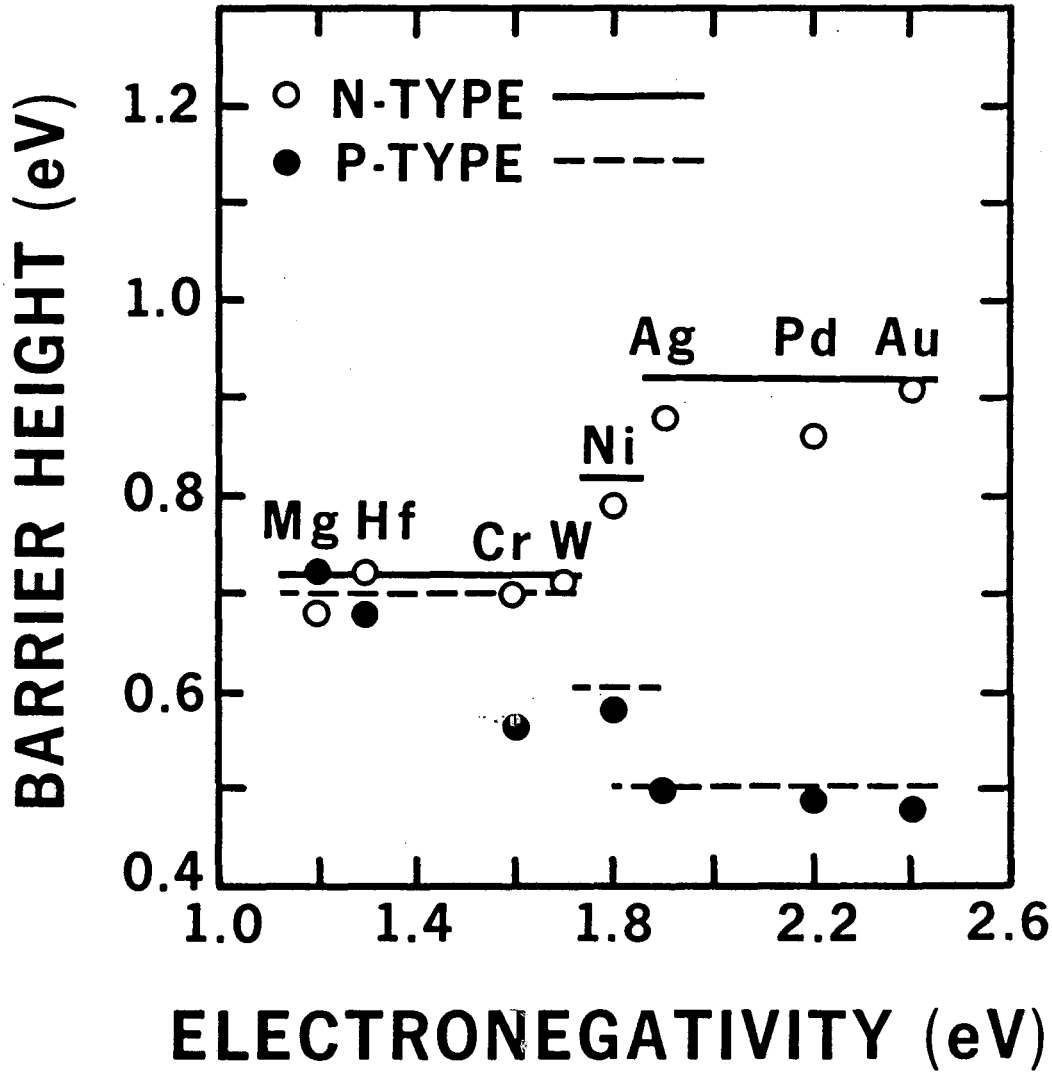

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Figure 2.

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BERKELEY, CALIFORNIA 94720