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Summary of Schottky barrier height data on epitaxially grown n- and p-GaAs

G. Myburg[a,*], F.D. Auret[a], W.E. Meyer[a], C.W. Louw[b], M.J. van Staden[b]

[a]*Department of Physics, University of Pretoria, Pretoria 0001, South Africa*
[b]*MATTEK, CSIR, P.O. Box 395, Pretoria 0001, South Africa*

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Abstract

The Schottky barrier height values, as determined by the current–voltage and capacitance–voltage techniques, of 43 metals which were fabricated by following the same cleaning procedure and using the same high-quality organometallic vapour phase epitaxially (OMVPE) grown (100) n-type GaAs material and 13 metals on molecular beam epitaxially grown (MBE) p-GaAs, are presented. Of all the metals involved in this study, Ga had the lowest mean Schottky barrier height of about 0.60 eV on n-GaAs and the highest on p-GaAs of 0.83 eV. Cu, Ag, Pt and Sb had the highest barrier heights of about 1 eV on n-GaAs. It was found that there exists no linear relationship between Schottky barrier height and metal work function as is suggested by the Schottky–Mott theory, if all 43 metals are taken into account. Similar results were obtained if the metal work function was replaced by the Pauling or Miedema electronegativities. In contrast with this, if only a selected group of metals is chosen and more specifically those with the higher melting points which were deposited by means of an electron gun, an approximately linear tendency does exist between Schottky barrier height and metal work function. From this linear dependency, the density of states was determined to be about 6×10^{13}/eV per cm^2 and the average pinning position of the Fermi level as 0.55 eV below the conduction band. © 1998 Elsevier Science S.A. All rights reserved

Keywords: Contacts; Electrical properties and measurements; Metallization; Schottky barrier

1. Introduction

The electron affinity, χ_s, of a semiconductor and the work function, ϕ_m, of a metal are important parameters in the formation of Schottky barrier diodes in terms of the Schottky–Mott and Bardeen theories. The work function of a metal is defined as the energy required to remove an electron from the Fermi level to a state of rest outside the surface. Metal work function consists of two components, a volume term and a surface dipole term. Similarly, the electron affinity of a semiconductor also contains a surface dipole term. These surface dipole terms are governed by the way the electronic charge is distributed at the surfaces of the solids and are therefore clearly influenced by the status of the surface. It is, however, impossible to measure the volume and the surface contributions of the work function separately. When a metal and semiconductor are brought into intimate contact, the atomic positions and the charge distributions of the surfaces in contact, will change in an unknown way and thus also the above-mentioned surface contributions. The Schottky–Mott theory can therefore not be expected to account well for barrier heights at such interfaces, since it assumes that ϕ_m and χ_s (or the difference between them) remain unchanged when contact is made. In an attempt to overcome this problem, it was suggested that the electronegativity of the metal be used, rather than its work function [1]. Electronegativity was described by Pauling as the ‘power’ of an atom to attract electrons to itself [2]. The concept of Pauling’s electronegativity [2–5] applies to individual atoms only and therefore does not take account of surface dipoles. Thus, there does not exist a linear relationship between work function and either the Pauling or Miedema electronegativities [6,8]. Although a number of theories and various mechanisms have been proposed in the literature, no definite explanation has yet emerged to explain the properties of metal–semiconductor contacts precisely. This might be due to the lack of detailed information on the nature of metal–semiconductor contacts on an atomic level.

* Corresponding author. Tel.: +27 12 4203508; fax: +27 12 3625288; e-mail: gmyburg@scientia.up.ac.za

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In this paper, results are presented of a systematic and the most comprehensive investigation ever conducted to determine the dependency of Schottky barrier height on the metal work function and the Pauling and Miedema electronegativities. During this study, 43 different metal/n-GaAs and 13 different metal/p-GaAs Schottky contact systems were evaluated on high-quality semiconductor material, after having undergone the same cleaning procedure prior to contact fabrication.

2. Experimental procedure

It is well known that the Schottky barrier height depends, amongst others, upon the quality of the semiconductor material, the method of surface preparation prior to metallization and the metallization itself. Therefore, only one thoroughly tested cleaning procedure, high-purity metals and high-quality semiconductor material were used during this study.

n-GaAs epilayer material with a free carrier concentration of $1 \times 10^{16}/cm^3$ (Si-doped) and thickness of about 8 μm, grown on n^+-GaAs substrate material by organometallic vapour phase epitaxy (OMVPE), was used as substrate material for Schottky contact fabrication. This epilayer material contained only the EL2 defect [8]. Ohmic contacts were formed prior to Schottky barrier diode fabrication by the deposition of Au/AuGe/Ni on the n^+-backsides of the wafers, followed by annealing at 450°C for 2 min in vacuum. After degreasing in TCE (trichloroethylene) and isopropanol, the samples were rinsed in deionised water, chemical etched in a freshly prepared solution of H_2O_2/NH_4OH/H_2O, in the ratio 1:3:150, followed by another rinse in deionised water before the oxide removal step (in HCl/H_2O, ratio 1:1) and final rinse of about 1 min in deionised water (18 MΩ cm). During the chemical etch step, the top section of the epilayer, about 300 nm thick, was removed. Semi-quantitative XPS analysis (2p3 peak of Ga and 3d peak of As) performed on the cleaned GaAs surface showed that it was As-rich (3d binding energy of 45 eV, which corresponds with As_2O_3).

The same cleaning procedure was followed for the p-GaAs. $4 \times 10^{14}/cm^3$ Be-doped MBE-grown p-GaAs was used as p-type material.

Directly after the final rinse in deionised water, the samples were either inserted by means of a fast introduction system into a turbomolecular pumped ultra-high vacuum system (used for the metals with the higher melting points) or a bell jar system. Circular metal contacts, 0.75 mm in diameter and between 50 and 500 nm thick (depending on the electrical conductivity of a specific metal, the lower the electrical conductivity, the thicker the contact to avoid the negative effects of spreading resistance), were deposited onto the GaAs substrates through a metal contact mask by

Table 1

Schottdky barrier heights according to (*I–V*) and (*C–V*) measurements for 43 metals on n-GaAs with a free carrier density of $1 \times 10^{16}/cm^3$; the darker the colouring, the higher the barrier height

.62eV 12 Mg .64eV						ϕ_{b0}^{I-V} Element ϕ_{b0}^{C-V}					.77eV Al .76eV	Si	P
20 Ca	.71eV Sc .69eV	.83eV Ti .82eV	.80eV V .80eV	.80eV Cr .83eV	.82eV Mn .83eV	.83eV Fe .84eV	.83eV Co .83eV	.83eV Ni .83eV	.99eV Cu .99eV	.81eV Zn .82eV	.59eV Ga .60eV	Ge	As
38 Sr	.71eV Y .70eV	.77eV Zr .77eV	.77eV Nb .79eV	.87eV Mo .87eV	Tc	.86eV Ru .91eV	.89eV Rh .90eV	.93eV Pd .93eV	.99eV Ag .98eV	.82eV Cd .82eV	.67eV In .68eV	.71eV Sn .70eV	.97eV Sb .99eV
56 Ba	La	.81eV 72 Hf .82eV	.78eV Ta 79eV	.79eV W .81eV	.87eV Re .88eV	Os	.90eV Ir .91eV	.99eV Pt .99eV	.92eV Au .92eV	Hg	Tl	.86eV Pb .86eV	.88eV Bi .89eV
58 Ce	.76eV Pr .75eV	.76eV Nd .75	Pm	.75eV Sm .74eV	Eu	.75eV Gd .74eV	.75eV Tb .75eV	Dy	.74eV Ho .74eV	.74eV Er .73eV	.72eV Tm .71eV	.67eV Yb .67eV	Lu

either electron beam [9] or resistive evaporation (low melting point metals such as Zn, Cd and Sn). Except for Hf (97%), V (99.8%) and the rare earth metals which may contain up to 2% Ta (according to the specifications of the manufacturers), the purity grade of all the other metals was equal to or better than 99.9%.

The values of the effective barrier height, ϕ_{b0}^{I-V} were determined by current–voltage (I–V) measurements at room temperature (about 298 K) and corrected afterwards for the effect of image force lowering [8,10]. An HP4140B pA meter/DC source was used to perform these measurements. Typical I–V curves were published elsewhere [9,11,12]. The I–V data was analysed under the assumption that the dominant current transport mechanism is thermionic emission. According to this theory, the J–V characteristics for $V > 3kT/q$ are given by the modified equation [6]:

$$J = J_0 \exp\left[\frac{qV}{nkT}\right], \text{ with } J_0 = A^* T^2 \exp\left[\frac{-q\phi_{e0}^{I-V}}{kT}\right] \quad (1)$$

where J = current density and J_0 the saturation current density. The effective barrier height is given by $\phi_{e0}^{I-V} = \phi_{b0}^{I-V} - \Delta\phi_{ifl}$, with $\Delta\phi_{ifl}$ the image-force lowering of the barrier ϕ_{b0}^{I-V}, n the ideality factor and A^* the effective Richardson constant [13]. The ideality factor is given by:

$$n = \frac{q}{kT}\left[\frac{\partial V}{\partial(\ln J)}\right] \quad (2)$$

An HP4192A impedance analyser, in conjunction with a high precision voltmeter, were used to perform the capacitance–voltage (C–V) measurements to obtain the barrier height values, ϕ_{b}^{C-V}. These measurements were performed at an oscillator frequency of 1 MHz. ϕ_{b}^{C-V} is given by the following equation [6]:

$$\phi_b^{C-V} = V_{d0} + \xi, \text{ with } \xi = \frac{kT}{q}\ln\left(\frac{N_c}{N_d}\right) \quad (3)$$

The diffusion voltage at zero bias, V_{d0}, is equal to $V_I + kT/q$, which is obtained from the intercept V_I of the curve $1/C^2$ versus V, while ξ represents the depth of the Fermi level below the conduction band in the neutral region of the semiconductor. N_c and N_d represent the effective density of states in the conduction band and the free carrier density of the semiconductor material, respectively.

At least eight contacts, obtained from two or more evaporation runs of the same metal, were measured (unannealed) in each case to obtain the mean Schottky barrier height values displayed in Tables 1 and 2. The largest statistical variation applicable to the various barrier height values was less than 2%. Mean values of the ideality factors of the 43 different metal Schottky contacts to n-GaAs used in this study are shown in Fig. 1. Note that in all cases, the ideality factors of the contacts used in this study, were less than 1.04. The barrier heights as obtained by (I–V) and (C–V) measurements corresponded very well (Fig. 2 and Table 1). The usefulness of these data lies in the fact that it was obtained from a relatively large number of metal Schottky contacts (which therefore included metals with a wide variation in properties, such as Mg and Pt) which were fabricated under the same cleaning procedure and on the same high-quality (100) n-GaAs and p-GaAs epi-materials, respectively, whereas most published data (tables of barrier height data) was compiled from data published by different authors and thus obtained under different processing conditions and materials [7,14], or it contained information on a much smaller number of metals [7,15,16].

Table 2

Schottky barrier height data for p-GaAs with a free carrier density of $4 \times 10^{14}/cm^3$

Zr	Sc	Hf	Al	Gd	Fe	Ru	Sm	Er	Nd	Sn	Yb	Ga
0.65	0.75	0.62	0.67	0.70	0.60	0.51	0.75	0.73	0.77	0.73	0.78	0.83

3. Results and discussion

If the simple Schottky–Mott model for Schottky barrier formation, given by:

$$\phi_b = \phi_m - \chi_s \quad (4)$$

is accepted, then a linear dependence should exist between the Schottky barrier height and the metal work function.[6,17–19] This model is a gross oversimplification of what is found in practice. From Fig. 3 it is clear that no such linear relationship exists for metal/n-GaAs Schottky contacts (as prepared under the given circumstances), if all 43 metals are taken into account. This fact corresponds with the graph (data contains large errors according to the error bars) published by Ghandhi [20]. It is, however, possible to obtain a linear relationship if only a selected group of metals is used. Cowley et al. [21] published similar results, but for a smaller selection of metals. Metals such as Y, Mg, Hf, Sc, and the rare earth metals with work functions smaller than the electron affinity of GaAs (4.07 eV), should actually form ohmic contacts to n-GaAs. Mn, with a work function of 4.10 eV, which is just slightly higher than the electron affinity of GaAs, should actually be added to this category. This is clearly not the case according to Fig. 3. (The work function values published in CRC Handbook of Chemistry and Physics, 1991 [22], for polycrystalline specimens, were used in this study.)

In the presence of interface states and a thin interfacial film, the barrier height is given by [6]:

$$\phi_b = \gamma(\phi_m - \chi_s) + (1-\gamma)(E_g - \phi_0) \quad (5)$$

with

$$\gamma = \frac{\epsilon_i}{\epsilon_i + q^2 \delta D_s} \quad (6)$$

E_g represents the band gap, ϕ_0, the so-called neutral level, δ and ϵ, the thickness and permittivity of the interfacial layer,

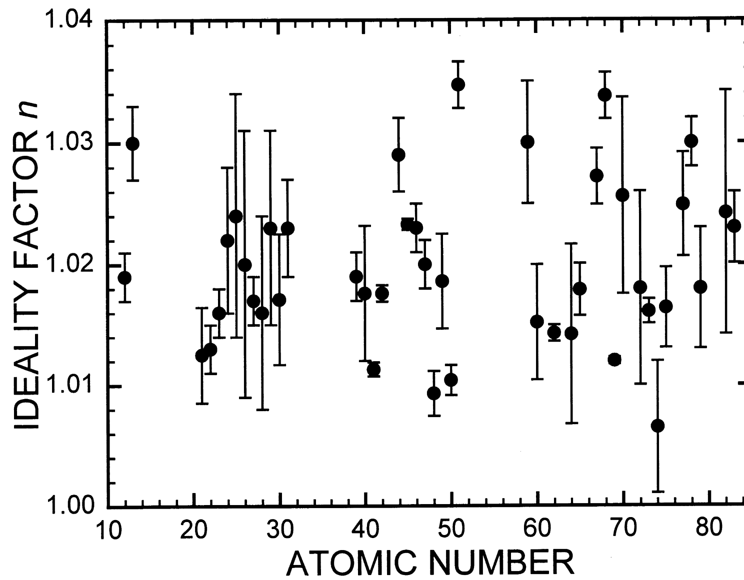

Fig. 1. The mean values (statistical errors included) of the ideality factors of the 43 different sets of metal Schottky contacts to n-GaAs used in this study.

and D_s the density of interface states per eV per unit area in the band gap [6,21]. The surface states are characterised by the neutral level, ϕ_0, such that all states below ϕ_0 are filled, while those above it are empty. Equilibrium is reached (Fermi level becomes constant throughout the semiconductor) when electrons from the semiconductor adjacent to the surface occupy states above ϕ_0. Thus, the surface becomes negatively charged and a depletion region is created within the semiconductor near the surface. If a metal is now brought into contact with the semiconductor, exchange of electrons takes place predominantly between the metal and the semiconductor surface states, while the depletion region charge remains practically unaffected — the Bardeen limit has been reached. Thus, if the value of D_s is large enough, Eq. (6) reduces to the Bardeen limit:

$$\phi_b \approx E_g - \phi_0 \qquad (7)$$

and the Fermi level becomes pinned at the neutral level, so that $E_f \approx \phi_0$. In this case, the Schottky barrier height is independent, or only weakly dependent on the work function of the metal.

In Fig. 3 the mean Schottky barrier height, is given as a function of metal work function. It is clear from Fig. 3 that there is no simple relationship between barrier height and metal work function as is suggested by Eq. (4). For example, the barrier height of Ag is almost the same as that of Pt, while the difference between their work functions is about 1.39 eV. Similar results were obtained if the metal work function was replaced by the Pauling or Miedema electronegativities (Fig. 4).

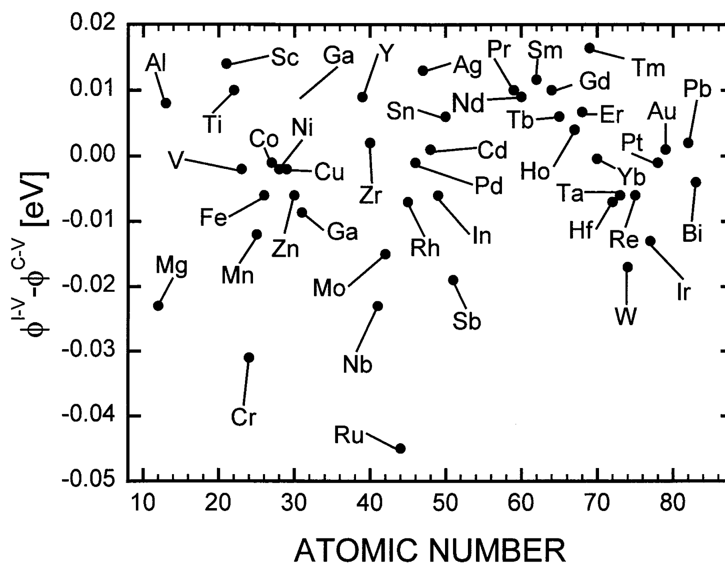

Fig. 2. The differences between the Schottky barrier heights as obtained by (*I–V*) and by (*C–V*) measurements.

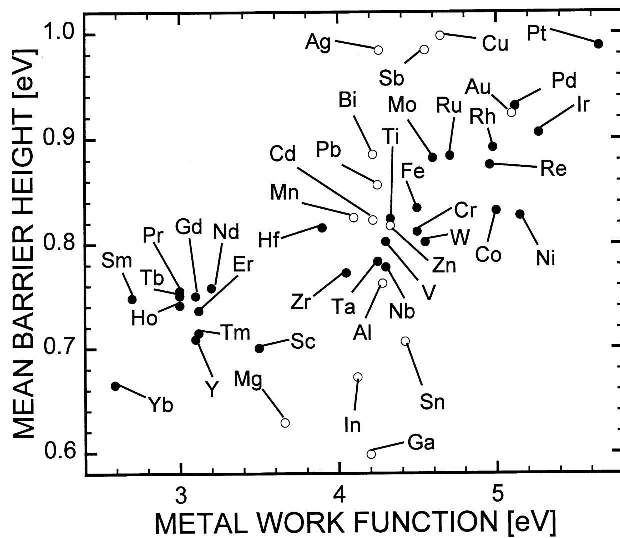

Fig. 3. The mean Schottky barrier height as a function of metal work function (Si doped n-GaAs with free carrier density of Nd = $1 \times 10^{16}/cm^3$).

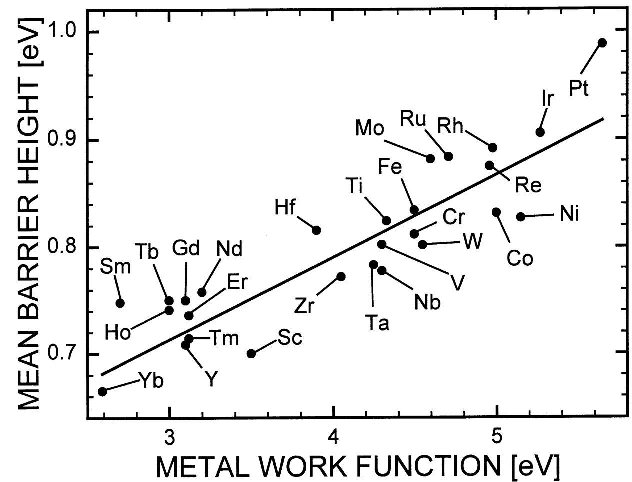

Fig. 5. The mean Schottky barrier heights of the metals deposited by means of an electron beam evaporator are shown as a function of metal work function (n-GaAs with free carrier density of Nd = $1 \times 10^{16}/cm^3$).

In contrast with this, if only a selected group of metals is chosen and more specifically those with high melting points (about 1000°C and above) which were deposited by means of an electron gun, an approximate linear relationship does exist between Schottky barrier height and metal work function, as is clear from Fig. 5. If the presence of significant concentrations of surface states at the metal–semiconductor interface are assumed, then from this linear dependency (Fig. 5) and Eqs. (5) and (6), the density of states, D_s, was determined to be about 6×10^{13}/eV per cm^2 and the average pinning position, ϕ_0, of the Fermi level as 0.55 eV below the conduction band.

Of all the metals involved in this study, Ga had the lowest mean Schottky barrier height of about 0.60 eV on n-GaAs and the highest on p-GaAs of 0.83 eV. Cu, Ag, Pt and Sb had the highest barrier heights of about 1 eV on n-GaAs. Due to the fact that the chemical properties of the rare earth metals are very similar, one would expect their barrier heights to be approximately the same. Yb is, however, an exception. It has a significantly lower barrier height compared to the other rare earth metals that were evaluated.

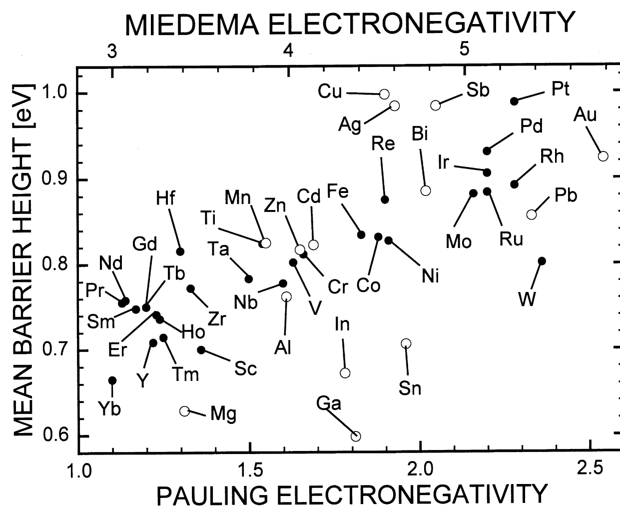

Fig. 4. The mean Schottky barrier height as a function of both the Pauling and Miedema electronegativities. (•) Electron beam evaporation; (◦) open circles, resistive evaporation.

4. Conclusions

The Schottky barrier height values, as determined by current–voltage and capacitance–voltage techniques, of 43 metals which were fabricated by following the same cleaning procedure and using the same high-quality OMVPE grown (100) n-type GaAs material (Si-doped, $10^{16}/cm^3$) and 13 metals on MBE grown p-GaAs, are presented in this paper. Of all the metals involved in this study, Ga had the lowest mean Schottky barrier height of about 0.60 eV on n-GaAs and the highest on p-GaAs of 0.83 eV. Cu, Ag, Pt and Sb had the highest barrier heights of about 1 eV on n-GaAs. Furthermore, it was found that there exists no linear relationship between Schottky barrier height and metal work function as is suggested by the Schottky–Mott theory, if all 43 metals are taken into account. Similar results were obtained if the metal work function was replaced by the Pauling or Miedema electronegativities. In contrast with this, if only a selected group of metals is chosen and more specifically those with high melting points which were deposited by means of an electron gun, an approximately linear relationship does exist between Schottky barrier height and metal work function. From this linear dependency, the density of states was determined to be about 6×10^{13}/eV per cm^2 and the average pinning position of the Fermi as 0.55 eV below the conduction band.

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