Compositional dependence of Schottky barrier heights for Au on chemically etched $In_xGa_{1-x}P$ surfaces

T. F. Kuech and J. O. McCaldin

California Institute of Technology, Pasadena, California 91125

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Measurements of the Au Schottky barrier height were carried out on thin films of n-$In_xGa_{1-x}P$, of various compositions epitaxially grown on n-GaAs substrates. Conventional C–V, I–V, and photo response techniques were used. The junction was formed by evaporating Au in an ion-pumped vacuum system onto a $In_xGa_{1-x}P$ surface which had been chemically etched ($5H_2SO_4$:$1H_2O_2$:$1H_2O$ at 40 °C for 90 s). Barrier heights determined from the I–V and photoresponse were found to be in good agreement while the C–V measurement encountered difficulties. The Au barrier, ϕ_p, to p-$In_xGa_{1-x}P$ was found to be independent of composition. The barrier, ϕ_p, was determined by the relation $\phi_p + \phi_n = \phi_g$ where ϕ_g is the bandgap energy and ϕ_n is the measured barrier to n-$In_xGa_{1-x}P$. It has been observed that the Au barrier height to p-type material for most compound semiconductors is determined by the anion, thus p-InP and p-GaP have the same Au barrier, about 0.76 eV. This dependence on the anion of the compound has now been seen to extend to the alloy system $In_xGa_{1-x}P$ measured here. While chemically etched specimens yielded diodes with reproducible barrier heights, diodes formed on surfaces which were untreated or cleaned only with organic solvents were of poor quality with varying barrier heights or even ohmic contacts.

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Gold/semiconductor interfaces provide some of the simplest examples of Schottky barriers. For common preparations, the barrier heights produced by Au contacts are usually a function of the anion of the semiconductor substrate, but not of the cation.[1] This dependence of the barrier height, sometimes called[2] the "common anion" rule, was reported to occur as well[3] for the vacuum/semiconductor interface, thus suggesting little chemical reactivity in Au Schottkies. Subsequent investigations,[4–7] however, have demonstrated a more complex situation, particularly with recent, sensitive surface preparations at UHV.

We consider here the common preparation of Schottky barriers at pressures $\lesssim 10^{-6}$ Torr (1.33×10^{-4} Pa) in the ternary system $In_{1-x}Ga_xP$. For the two end points, $x = 0$ and $x = 1$, the barrier height, ϕ_p, on p-type material is known to be ~0.76 eV. We wish to determine whether ϕ_p remains constant for intermediate compositions. An analogous study of the corresponding arsenide ternary, $In_{1-x}Ga_xAs$,[8] showed ϕ_p to be independent of composition, as would be expected by the common anion rule. A contrary result has been obtained, however, in ternaries involving aluminum. In the alloy system n-$Ga_{1-x}Al_xAs$, $\phi_p = \phi_g - \phi_n$ was found to increase linearly with aluminum content.[2]

$In_{1-x}Ga_xP$ and the quaternary formed by As addition has been investigated as a potential semiconductor laser material for use in fiber optics communication. The bandgap varies with composition from the direct gap of pure InP which has a value of 1.35 eV to the indirect gap of GaP at 2.24 eV. The alloy system undergoes a direct to indirect transition at a composition of 74 mol % GaP. Since the Au barrier to p-InP and to p-GaP is the same, it is expected that in this alloy system the common anion trends should be observed.

The Au Schottky barrier height was measured on 1–2 μm films of n-$In_{1-x}Ga_xP$ of various compositions epitaxially grown by LPE on ⟨100⟩ n-GaAs substrates. Bulk samples of n-InP were also used in the subsequent measurements. All the specimens were first cleaned in a series of organic solvents (TCE, acetone, and methanol) and then chemically etched in a solution of $5H_2SO_4$:$1H_2O_2$:$1H_2O$, cooled to 40°C, for 90 s. After etching, the samples were rinsed in distilled water and dried. The etching rate of the acid solution was found to be 200–500 Å/min. Ohmic contacts were made to the GaAs substrate before etching by evaporating a Au–Ge eutectic and annealing in forming gas (5% H_2 − 95% N_2) at 380°C for 90 s. The etched samples were then placed in an oil free ion pumped vacuum system. Gold evaporated through a stainless steel mask formed 160 μm diameter dots on the sample surface. The vacuum system pressure was less than 10^{-6} Torr (1.33×10^{-4} Pa) as measured at the ion pump during evaporation. Samples of n-InP were also prepared by cleaving in air prior to the Au evaporation. In the case of n-InP, samples prepared by these two methods produced similar barrier heights.

The chemical composition of the epitaxial layers was determined by photoluminescence and electron microprobe measurements. The electron beam energy was 15 keV and the data was reduced by the Bence and Albee technique.[9] The two methods agreed well. Estimated error bars are shown in Fig. 3.

Electrical and photoresponse measurements were then carried out on the resulting structures. Reverse bias capacitance–voltage and forward bias current–voltage characteristics were both measured.

The forward bias I–V characteristics were measured over many decades of current and were fitted to an equation of the form, $J = J_0(e^{qv/nk_BT} - 1)$, where J is the current density and

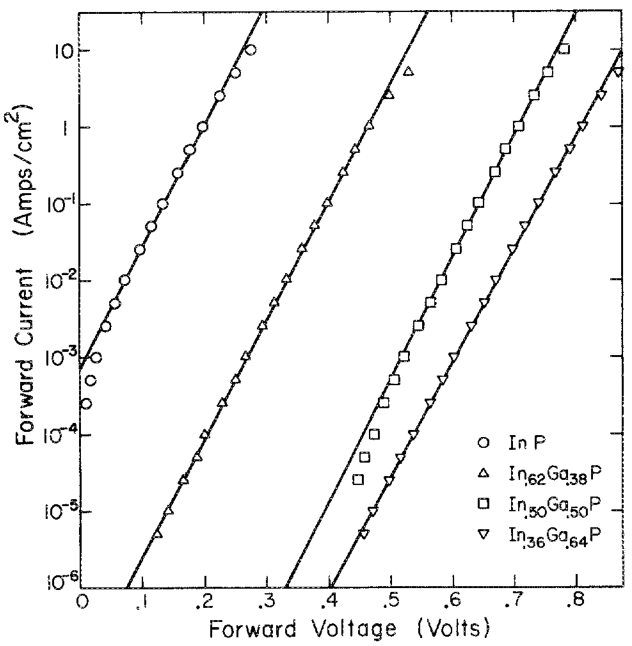

FIG. 1. The forward bias current–voltage characteristics of Au on $In_xGa_{1-x}P$ Schottky barriers. The approximate area of the Au dots was 2×10^{-4} cm^2.

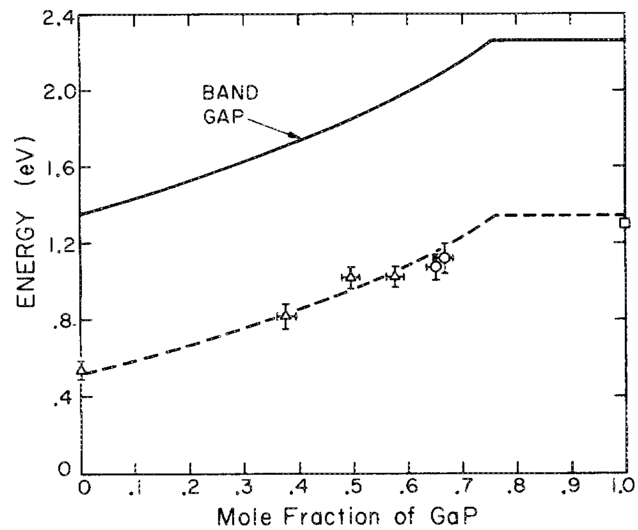

FIG. 3. Measured Au Schottky barrier heights as a function of mole fraction of GaP, x in $In_{1-x}Ga_xP$. Δ indicates barrier heights obtained from diodes having a quality factor $n \leq 1.1$, O indicates diodes with $n \leq 1.2$, and □ is the Au on GaP barrier height reported by Mead *et al.*[15] Dashed line is band gap -0.76 eV, i.e., barrier height expected by the common anion rule.

n is the quality factor. If n is close to unity then the results of thermionic emission theory apply, such that $J_0 = A^*T^2e^{-\phi_n/K_BT}$, where A* is the modified Richardson constant ($A^* = 120\,(m^*/m_0)(A/\mathrm{cm}^2)$ and ϕ_n is the barrier height.[10] Typical I–V characteristics of samples of various alloy compositions are shown in Fig. 1. Only diodes having a quality factor $n \leq 1.1$ were used in the subsequent analysis except where noted.

The photoresponse measurements were performed by illuminating the metal–semiconductor interface through the GaAs substrate with monochromatic light. A broad spectrum tungsten lamp and a Gaertner monochromator were used as a light source. The photoresponse as a function of incident photon energy at various alloy compositions is shown in Fig. 2. The photocurrent was found to be of the form $J\alpha(h\nu - \phi_n)^2$ as expected for emission from the metal into vacuum or semiconductor.[11]

The barrier height as determined by I–V and photoresponse methods is shown in Fig. 3 as a function of composition. The estimated error in the barrier height is indicated by error bars. The barrier heights shown here have not been corrected for the Schottky lowering effect. Since the sample doping is of the order 10^{16}–10^{17} per cm^3, the decrease in barrier height would be 20–50 meV. The bandgap of $In_{1-x}Ga_xP$ is also indicated on this figure by a solid line. All barrier height measurements were done on direct gap material.

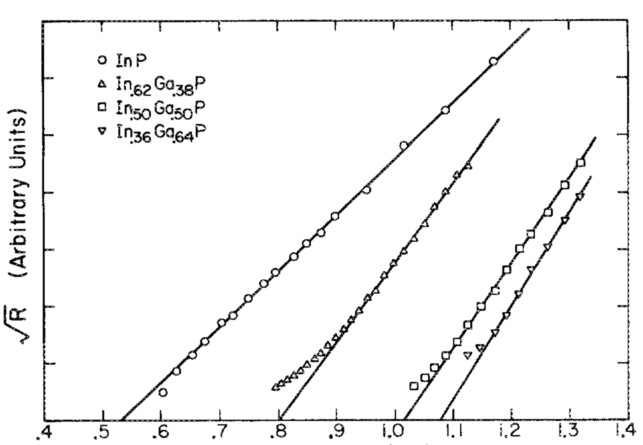

FIG. 2. The photoresponse as a function of incident photon energy at various alloy compositions for Au Schottky barriers on n-$In_xGa_{1-x}P$.

Barrier heights deduced from I–V and photoresponse methods were found to be in good agreement while the C–V measurement was found to be unreliable. In $_{1-x}Ga_xP$ is lattice matched to GaAs at $x = 0.51$.[12] The capacitance method may be affected by bulk crystal defects in the epitaxial layer induced by the lattice mismatch of the epitaxial material to the GaAs substrate making the results difficult to interpret. High dislocation densities have been reported in $In_{1-x}Ga_xP$ grown on GaAs at compositions away from the lattice matched value.[12] Good agreement between barrier heights as deduced from the capacitance method and the other two methods was found only near the lattice matched composition.

An increased deviation from ideal thermionic behavior ($n = 1$) in the I–V characteristic was also observed as the sample composition was shifted away from the lattice matched composition. This is illustrated in Fig. 4 where the quality factor, n, increases with lattice mismatch, $|(a_{\mathrm{epi}} - a_{\mathrm{sub}})/|$, where a_{epi} and a_{sub} are the lattice parameters of the epitaxial and substrate materials, respectively. The value of a_{epi} was calculated using Vegard's law.[13]

While acid etched samples gave reproducible barrier heights with nearly ideal diode characteristics, Schottky diodes fabricated on samples of $In_{1-x}Ga_xP$ which had been cleaned only by organic solvents often resulted in anomalous behavior. Barrier heights of such diodes were found at times to give higher barriers than the acid etched samples, while other such samples yielded very low or zero barriers. Such results were usually nonreproducible, thus requiring the use of the acid etch.

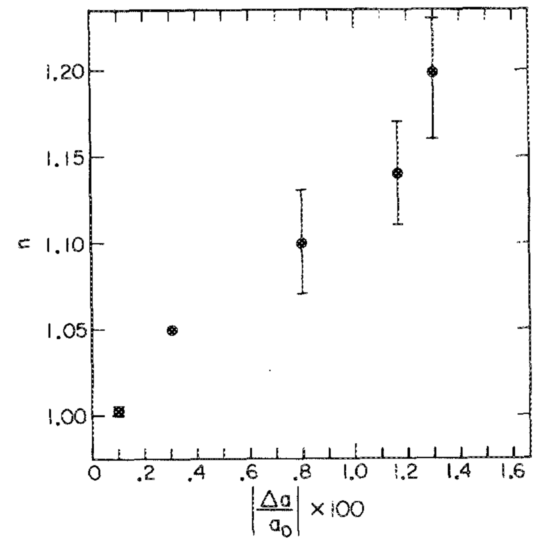

FIG. 4. The quality factor, n, determined by fitting the measured current density to the function $J = AT^2 e^{qV/nK_BT}$, is plotted as a function of lattice mismatch between the $In_xGa_{1-x}P$ epilayer and GaAs substrate. The lattice parameter was calculated using Vegard's law.

According to the common anion rule, ϕ_p, being equal to the energy difference between the bandgap and ϕ_n which was measured here, should be a constant. This is the case for $In_{1-x}Ga_xP$ where the barrier to n-type material is fixed relative to the conduction band minimum. This is indicated by the dashed line in Fig. 3. Deviations from ideal thermionic behavior ($n > 1$) seen at the larger values of lattice mismatch tend to give slightly lower values for the barrier height as calculated from the I–V characteristic than in the ideal thermionic case. This may give rise to the apparent slight deviation from the common anion rule found at the gallium rich alloy compositions.

It has then been found that if the common anion rule applies to two compound semiconductors, such as InP and GaP, then the rule can be extended to an alloy mixture of those two compounds. This has been seen in the alloy systems investigated so far. It is expected that the $In_{1-x}Ga_xSb$ system will also follow these common anion trends. The extension of this work to quaternary systems has yet to be investigated.

It has been suggested that information derived from Schottky barrier measurements could also prove useful in estimating band edge discontinuities in heterostructures.[1]

Since the valence band position relative to the Au fermi level has been observed to be determined by the anion of the semiconductor compounds, the valence band discontinuity, ΔE_v, of compound semiconductor heterostructures composed of alloys or compounds following the common anion rule may be independent of the respective cations. Thus, one might expect the valence band discontinuity, ΔE_v, of $In_{1-x}Ga_xP_{1-y}As_y$–InP heterostructure to be independent of x. Using a linear interpolation for an estimate of the valence band position with respect to Au of $In_{1-x}Ga_xP_{0.71}As_{0.13}$, one would expect that $\Delta E_v \simeq 70$ meV. Recent experiments[14] in this system indicate $\Delta E_v = 80$ meV.

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