Photoemission spectroscopy of Al$_{0.27}$Ga$_{0.73}$As:As photodiodes

D. T. McInturff, J. M. Woodall, A. C. Warren, N. Braslau, G. D. Pettit, and P. D. Kirchner
IBM Research Division, P.O. Box 218, Yorktown Heights, New York 10598

M. R. Melloch
School of Electrical Engineering, Purdue University, West Lafayette, Indiana 47907

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We report on photoemission measurements of MBE-grown Al$_{0.27}$Ga$_{0.73}$As p-i-n structures in which the optically active insulating layers contain arsenic precipitates (Al$_{0.27}$Ga$_{0.73}$As:As). Al$_{0.27}$Ga$_{0.73}$As:As layers were formed by low temperature growth of Al$_{0.27}$Ga$_{0.73}$As followed by a high temperature anneal. GaAs layers grown in this way have been reported to be sensitive to subband-gap light. A Fowler plot constructed from an internal photoemission measurement gave a barrier height of 0.93 eV. We compare this result with the barrier height of arsenic in GaAs that was found to be 0.7 eV using the same structure and measurement scheme. This result demonstrates that the barrier height of embedded metallic arsenic clusters in Al$_{x}$Ga$_{1-x}$As is consistent with the heterostructure conduction band offset and can be selected by changing the composition of the host material.

Low temperature GaAs (LT-GaAs), an arsenic rich form of GaAs that results when GaAs is grown at 200 °C by molecular beam epitaxy (MBE), first attracted attention as a means of eliminating back- and side-gating in GaAs metal-semiconductor field-effect transistors. Further studies have shown that this material, when subsequently annealed at 600 °C, is transformed into a new phase of GaAs containing a high density ($1 \times 10^{17}$/cm$^3$) of arsenic precipitates (GaAs:As). It has been reported that GaAs photodiodes with active layers consisting of GaAs:As are sensitive to 1.3 μm light. Previously, in an experiment employing a positive-intrinsic-negative (p-i-n) structure with the i-layer consisting of GaAs:As, it was shown that embedded arsenic precipitates act as internal Schottky barriers with a measured barrier height of 0.7 eV. This reinforced an earlier explanation of the apparent compensation of both p and n type GaAs:As by Warren et al. that suggested the high resistivity was due to depletion regions surrounding the buried arsenic precipitates. In addition, the optical sensitivity to subband-gap light of GaAs:As was explained by emission from buried metallic clusters. It was proposed that the barrier height and hence optical sensitivity could be varied by changing the host alloy composition.

The Schottky model for metal/semiconductor systems predicts that the barrier height will increase as the difference between the metal work function and the electron affinity of the semiconductor is increased. For metal/GaAs systems, the barrier height has been shown to vary with the metal work function, but only by going to the extreme effort of in situ metal deposition in an ultrahigh vacuum MBE system. Usually, the barrier height for a metal/GaAs is pinned at around 0.8 eV regardless of metal work function. However, in experiments where the metal work function is kept constant and the electron affinity is varied by changing the alloy composition, the Schottky effect is easily observed. In this letter we measure, by internal photoemission, the barrier height of arsenic precipitates in Al$_{0.27}$Ga$_{0.73}$As, which has a lower electron affinity than GaAs. Using this technique, we measure a barrier height for the Al$_{0.27}$Ga$_{0.73}$As:As system of 0.93 eV.

Figure 1 shows a schematic cross sectional view of the grown and processed Al$_{0.27}$Ga$_{0.73}$As:As p-i-n photodiode. The layers were grown on (100) oriented Si-doped GaAs substrates. The film was grown using As$_2$, two Ga effusion furnaces, and one Al effusion furnace, and one Al effusion furnace. Si and Be are the n- and p-type dopants, respectively. All layers were grown at a rate of 1 μm/h and with a group V to group III beam equivalent pressure ratio of 20. An n-GaAs buffer layer was first grown at 600 °C followed by a 0.1 μm n-AlGaAs layer; both layers were doped at $1 \times 10^{18}$/cm$^3$. The growth was interrupted and the substrate temperature decreased to 250 °C while maintaining the As$_2$ flux. After attaining a substrate temperature of 250 °C, a 1 μm i-Al$_{0.27}$Ga$_{0.73}$As layer was grown. Again, the growth was interrupted and the substrate temperature was raised to 600 °C while maintaining the As$_2$ flux. After reaching 600 °C, a 0.1 μm p-Al$_{0.27}$Ga$_{0.73}$As layer and a 0.4 μm p-GaAs layer were grown. Both of these layers were doped at $1 \times 10^{18}$/cm$^3$. 

![FIG. 1. Schematic of MBE grown Al$_{0.27}$Ga$_{0.73}$As p-i-n photodiode. Arsenic clusters in i-layer act as buried Schottky barriers.](image-url)
Finally, the structure was capped with a $p$-GaAs layer doped at $5 \times 10^{19}/\text{cm}^3$. After growth, the film was annealed in the MBE chamber at 600 °C for an additional 30 min under the As$_2$ flux. Transmission electron microscopy (TEM) has confirmed that arsenic clusters exist at a concentration of $1 \times 10^{16}/\text{cm}^3$ in AlGaAs that has been grown in this way. The devices were fabricated as reported earlier and had a dodecahedral current voltage characteristic. A low reverse bias leakage current was observed due to the arsenic precipitates in the thick $i$-Al$_{0.27}$Ga$_{0.73}$As layer which acted as current sinks.

Internal photoemission measurements were performed on the structure. The experimental setup has been described previously. The photoresponse was taken over the wavelength range $1.1 \mu \text{m} < \lambda < 1.6 \mu \text{m}$. Figure 2 shows the Fowler plot of the photoresponse data taken on the Al$_{0.27}$Ga$_{0.73}$As:As $p$-$i$-$n$ photodiode. The extrapolation of the Fowler plot data to zero photoresponse for the photodiode gives a barrier height of 0.93 eV. Since the measurement was performed at room temperature, the tail observed toward the low energy end of the spectrum can be attributed to Fermi broadening of the carriers in the arsenic wells. That is, the effect of the optical excitation is being overwhelmed by thermal excitation of the carriers. It is expected that this can be reduced by performing the measurement at lower temperatures. Such a measurement would result in an extended linear portion of the Fowler plot which, if performed at near absolute zero, would intercept the energy scale at the barrier height of the buried Schottky barriers. In earlier studies of conventional Schottky barriers to GaAs, it has been observed that Au, which has a relatively large work function, typically gives a Schottky barrier height of about 0.9 eV when extraordinary measures are not taken to avoid air exposure. Similarly, when Au is deposited on Al$_{0.27}$Ga$_{0.73}$As, the barrier height has been found to be 1.1 eV. Although the absolute barrier heights are lower than what would be expected from Schottky theory, the change in barrier height between Au/ Ga$_{0.73}$Al$_{0.27}$As and Au/GaAs is about 0.20 eV and is nearly that expected for a change in barrier height dominated by a change in electron affinity. Since our internal photoemission results show a barrier height change of 0.23 eV between Ga$_{0.73}$Al$_{0.27}$As:As and GaAs:As, the change in electron affinity appears to dominate our observed barrier height change.

In contrast to the current-voltage measurements quoted above, where the Au/Al$_{0.27}$Ga$_{0.73}$As interfaces are not necessarily well understood, the Al$_{0.27}$Ga$_{0.73}$As:As system has a very well defined interface. This is because there is no possibility of air exposure when the buried interfaces are formed. The embedded arsenic is really the metal, rather than being a mixed phase of the intended metal, along with arsenic and oxygen. Thus, these experiments give an absolute value for what can be expected from contaminant free arsenic/GaAs and arsenic/AlGaAs interfaces and provide a baseline for the comparisons made above. These results strengthen the case for work function domination of conventional Au/n-GaAs and Au/n-AlGaAs contacts by virtue of the fact that the presence of arsenic is commonly observed to uniformly lower measured barrier heights of Au on n-Al$_{0.27}$Ga$_{0.73}$As:As from what would be expected from pure Schottky theory.

In summary, photoemission spectroscopy was performed on a $p$-$i$-$n$ structure with Al$_{0.27}$Ga$_{0.73}$As:As forming the device active layer. The device had a photoresponse similar to that of a previously measured structure with GaAs:As forming the active layer. The shift in the measured barrier height between the two structures is consistent with the change in the electron affinity of the host alloy. When comparisons are made between these measurements and current-voltage measurements of Au/n-GaAs and Au/n-AlGaAs, we find consistency in the arguments that arsenic precipitates rather than arsenic antisite defects dominate the behavior of our photodiodes and that measured barrier heights of conventional GaAs and AlGaAs Schottky diodes are dominated by the work function of excess arsenic found at the interface. M. R. Melloch would like to acknowledge support by the Air Force Office of Scientific Research under Grant No. F49620-93-1-0031.