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EFFECT OF Sb ON THE PROPERTIES OF GaInP TOP CELLS*

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ABSTRACT

It is well known that the efficiency of GaInP/GaAs tandem solar cells is limited by the band gap of the GaInP top cell, which, in turn, is determined by the degree of compositional ordering in GaInP base layer. Attempts to raise the band gap by the addition of Al to the top cell have met with limited success due to the strong affinity between Al and oxygen. Here we investigate a different approach. It has been shown that the presence of antimony on the surface of GaInP during its growth suppresses the ordering process and increases the band gap. In this paper, we study the effects of Sb on the properties of GaInP top cells. We show that, in addition to raising the band gap of GaInP, it also increases the incorporation of Zn and changes the relative incorporation of Ga and In. These effects depend strongly on the substrate orientation, growth temperature and rate, and the Sb/P ratio in the gas phase. We show that the band gap of the GaInP top cell (and the Voc) can be increased without reducing the minority carrier collection efficiency. The implications of these results are presented and discussed.

INTRODUCTION

The efficiency of a GaInP/GaAs tandem solar cell depends on the thickness and band gap of the GaInP top cell.[1, 2] For the growth conditions typically used to produce high quality electronic properties, the band gap of GaInP at a composition lattice-matched to GaAs is in the range of 1.8 eV. This band gap corresponds to partial ordering of Ga and In on the group III lattice sites. To achieve current matching with a 1.8eV band gap requires that the GaInP be thinned to some finite thickness on the order of 1μm.[1-4] However, for optimal efficiency both the thickness and band gap of the top cell should be increased. The highest efficiency occurs for a top-cell band gap of 1.9 eV, which, for GaInP, occurs when the Ga and In atoms are randomly located on the group III sublattice. Efforts to grow "disordered" GaInP with a 1.9 eV band gap have met with mixed success. One very effective way to decrease the ordering is to grow on GaAs(001) substrates with a X˚ miscut towards [110] (abbreviated X˚A) where X is in the range of 2˚ to 15˚.[5] Takamoto and coworkers used this fact to achieve an efficiency of 30.3%.[6] It has also been shown that the addition of various dopants can hinder the ordering process and increase Eg. For shallow dopants, the band gap increases only for dopant levels that adversely affect the minority carrier transport properties.[7]

Antimony, on the other hand, can be used to suppress the ordering process[8, 9] A plot of this effect is show in Fig. 1. And since Sb is isoelectronic with P in GaInP, its effect on the minority carrier transport properties may be minimal. Hence it is the intent of this paper to examine the effect of Sb on the properties of GaInP top cells.

EXPERIMENTAL DETAILS

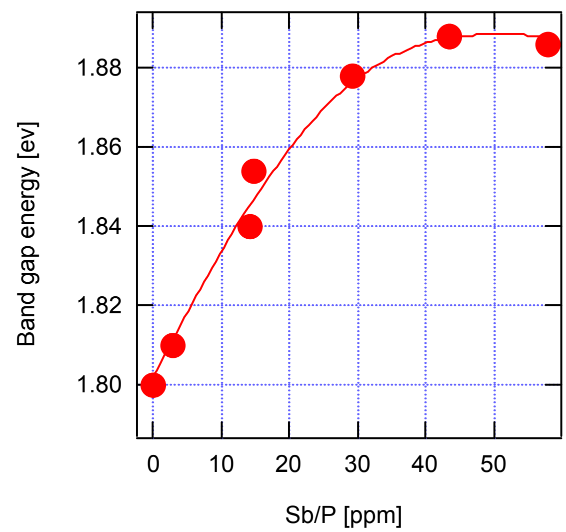

Figure 1 Band gap of GaInP as a function of Sb/P gas phase mole fraction. Substrate was GaAs(001) 6˚B. The growth temperature, rate and V/III ratio were 620˚C, 5 μm/hr, and 300, respectively.

All epilayer structures and devices were grown by low-pressure metal-organic chemical vapor deposition (MOCVD) using as sources triethylantimony (TESb), triethylgallium (TEG), trimethylindium (TMI), trimethylaluminum (TMA), phosphine (PH_3), and arsine (AsH_3).

The cells were a simple n-on-p structure with a Zn-doped AlGaInP back surface field (BSF) and a Se-doped AlInP window layer and GaAs contacting layer. They were grown on Zn-doped GaAs substrates. The substrate was GaAs(001) misoriented 6˚ towards (111)B (6˚B). Unannealed electroplated gold was used for the front and rear contacts. Unless otherwise stated, the cells were grown at 620˚C, at a rate of 5 μm/hr with a V/III ratio of 300.

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The composition of ternary layers was determined from high-resolution x-ray diffraction measurements and fitting the results using a dynamical x-ray diffraction model from Bede Scientific, Inc.

The carrier concentration in the GaInP base and similar layers was obtained from capacitance-voltage (CV) measurements.

Behavior of Sb-doped GaInP

Besides the band gap there are a number of other aspects of GaInP that are affected by the presence of Sb. In Fig. 2 we show the effect of Sb on the composition x of $Ga_xIn_{1-x}P$. For the B-miscut substrates the alloy becomes Ga-rich with Sb. For singular (001) surfaces there is virtually no effect and for substrate misoriented toward

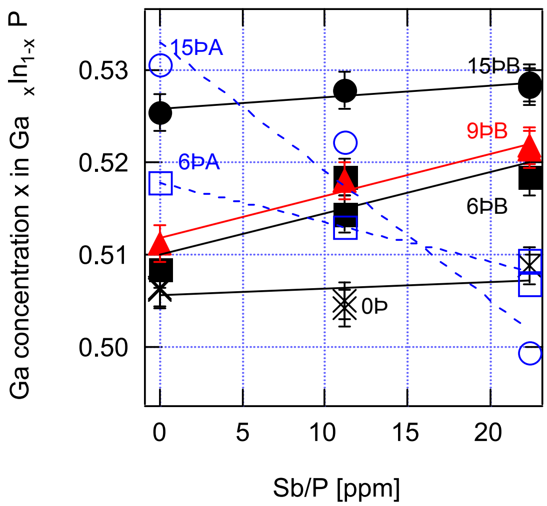

Fig. 2 Composition of $Ga_xIn_{1-x}P$ vs. Sb/P in the gas phase for various substrate orientations. The growth temperature is fixed at 620˚C, the V/III at 500 and the growth rate at 4.8 µm/hr.

(111)A, the alloy becomes In-rich with Sb. These results have implications concerning the ordering mechanism as discussed below.

The Zn incorporation also increases with Sb concentration, as shown in Fig. 3. As the Sb/V ratio is increased from 0 to 30 ppm, it increases by a factor of ~2, and for 25 ppm < Sb/P < 60 ppm, the Zn incorporation is approximately constant.

The Se incorporation decreases with Sb concentration as shown in Fig. 4. Here we plot the sheet resistance of a Se-doped emitter of an n/p GaInP top cell. (Direct measurement of the electron concentration confirms this result.) Antimony and Se compete with P for group V sites on the surface during growth. Increasing the TESb or PH_3 partial pressure will lower the Se incorporation. Hence it may be desirable to lower the TESb flux during the growth of the emitter.

Antimony has a large effect on the morphology of the growing surface. This is particularly evident for layers grown on singular (001) surfaces. Without Sb, the (001)

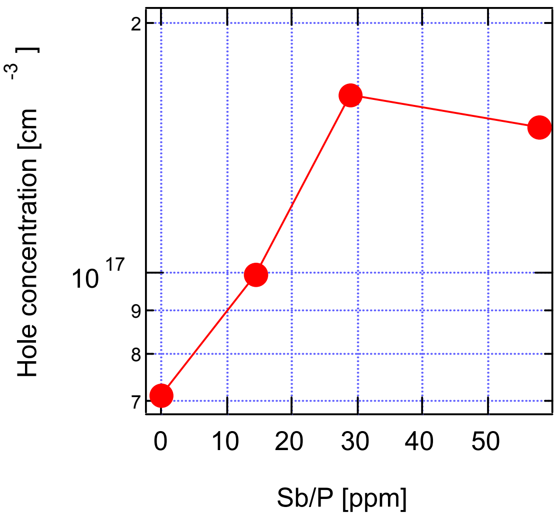

Fig. 3 Effect of Sb on the acceptor concentration in the Zn-doped base of an n/p GaInP top cell.

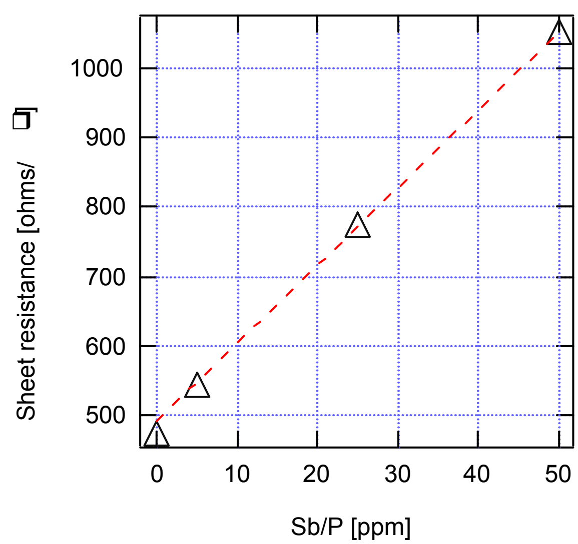

Fig. 4 Sheet resistance of a Se-doped GaInP emitter as a function of antimony to phosphorus ratio. The emitter thickness is ~100 nm. The growth rate, temperature and V/III ratio are 5µm/hr, 620˚C and 600.

surface is composed of asymmetric hillocks, bounded by low angle (4˚) B-type facets, similar to that observed by Friedman *et al.* for ordered GaInP.[10] At high Sb concentrations the surface becomes very flat with wide (001) terraces separated by monolayer high steps (0.28 nm), as shown in Fig. 5.

This result strongly suggests that the main effect of Sb is to modify the step flow properties of the surface. However, the amount of Sb needed has been a matter of debate. The current literature suggests that there is closer to a full monolayer of Sb on the surface.. It should not take much Sb on the surface to modify the step flow if it were mainly concentrated on the steps. With this in mind we used the model of Muraki *et al.*[11] and SIMS to

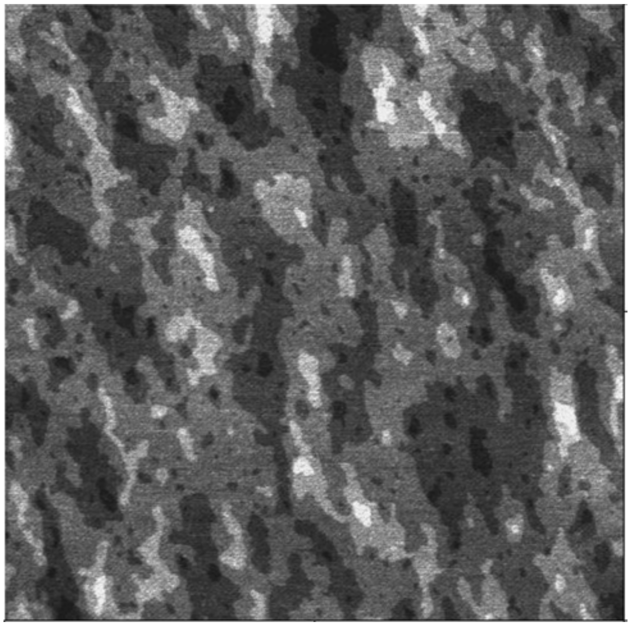

Fig. 5 Atomic force microscopy image of singular GaInP(001) growth surface. The image size is 2 μm x 2 μm. The height difference between distinct shades of grey is 0.28 nm, or half the lattice constant of GaInP. The growth temperature, rate and V/III were 620˚C, 2 μm/hr and 450.

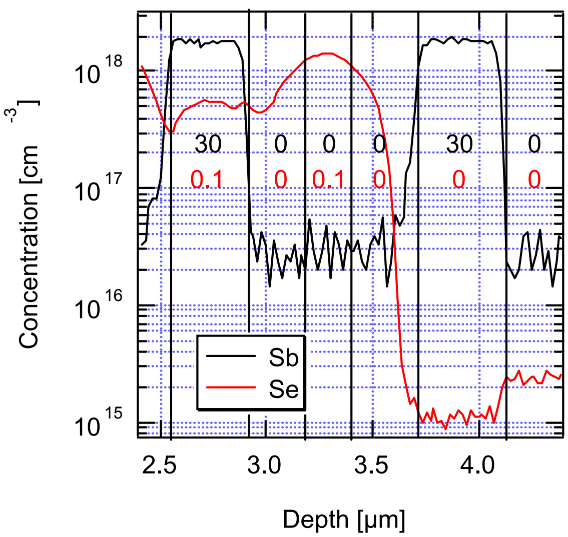

Fig. 6 SIMS profile of a GaInP layer grown with various combinations of Se and Sb. The black vertical lines are boundaries between various layers. The black(red) numbers refer to the input Sb(Se)/P ratio. Note that the Se incorporation decreases by a factor of ~2 in the presence of Sb. Analysis of the Sb rise(fall) profiles yields an Sb surface concentration Θ_{Sb} = 0.003(0.006).

measure the Sb surface concentration under typical top-cell growth conditions. The result is that the Sb surface concentration Θ_{Sb} in the range of 0.003 to 0.006, much less than a monolayer (see Fig. 6).

Sb-doped GaInP Solar Cells

A series of GaInP cells were grown with a variable amount of Sb present in the vapor phase during growth. All the cells had a nominal base thickness of 2μm and were grown at ~620˚C with a V/III of 300 and with a growth rate of 5 μm/hr. Both Eg and Voc increase with Sb/V, as shown in Fig. 7. The Voc, however, increases at a slower rate relative to Eg. This may indicate that the minority lifetime in the cell is decreasing with Sb, as seen by Fetzer *et al.*[9] The Jsc decreases with Sb/P (and Eg). However, the rate is slower than that expected theoretically, as shown in Fig. 8.

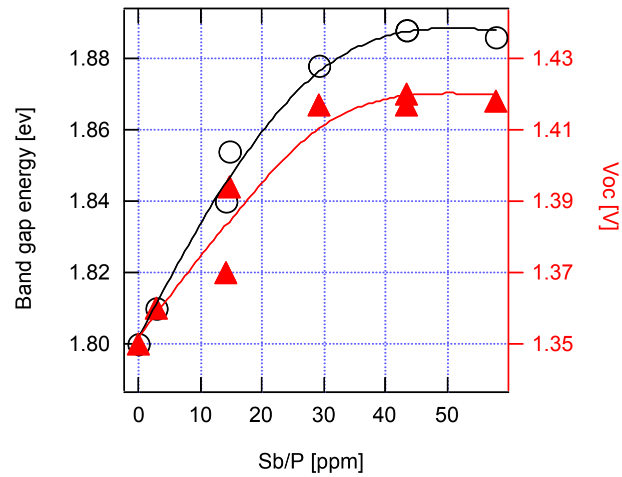

Fig. 7 Band gap energy and Voc of GaInP solar cells (with no ARC) versus the Sb/P in the gas phase during growth of the base.

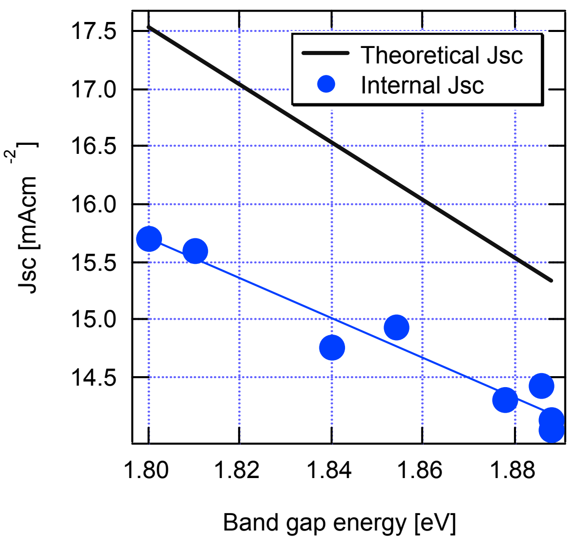

Fig. 8 Theoretical and measured internal Jsc vs. band gap energy for the series of GaInP presented in Fig. 5.

Sb-doped GaInP/GaAs TANDEM CELLS

An Sb-doped GaInP/GaAs tandem cell was fabricated with the top cell doped with Sb/P = 58 ppm,giving a band gap of 1.89 eV. It was lattice matched to underlying GaAs to within 0.01%. The thickness of the top cell base and emitter were 2 μm and 0.1 μm, respectively. The base of the GaAs bottom cell was 2.5-μm-thick and doped with Zn at a level of ~2e17 cm^{-3}. A Zn-doped $Al_{0.25}Ga_{0.25}In_{0.5}P$ layer was used as the BSF for both subcells. The tunnel junction was a Se-doped GaInP/C-doped AlGaAs heterojunction similar to that proposed by Bedair *et al*.[12] The cell was patterned with a concentrator grid. The total and active areas of the device were 0.116 cm^2 and 0.103 cm^2, respectively. A summary of the 1-sun AM1.5G results is shown in Table 1.

The Voc of this device is equal to that achieved by Takamoto *et al*.[6] However, because of the large busbar obscuration, 1-sun Jsc for this cell is correspondingly low. Conversely, the active area Jsc for the top and bottom cells indicates that with appropriate grid design, the efficiency of this cell should exceed 31%.

Table 1 Device parameters for an Sb-doped GaInP/GaAs tandem cell grown on GaAs.

Voc [V]	FF	Jsc, Total area [$mAcm^{-2}$]	Jtop, active area [$mAcm^{-2}$]	Jbottom, active area [$mAcm^{-2}$]
2.48	0.87	12.4	14.8	14.9

CONCLUSION

The properties of Sb-doped GaInP are very intriquing and yield clues as the fundamental mechanism of ordering in GaInP. Antimony is also an effective way to increase the band gap and Voc of a GaInP solar cell. This has important implications for very high efficiency two- and three-junction solar cells for concentrator applications.

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