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Gettered GaP Substrates for Improved Multijunction Solar Cell Devices

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We report on the characterization of gettered *p*-type GaP substrates for application in high-efficiency multijunction solar cells. A commercial zinc-doped GaP substrate was divided, with one piece soaked in a phosphorus-saturated gallium-aluminum melt at 975°C. Low-temperature continuous-wave photoluminescence indicated a significant decrease in deep-level impurity peaks due to oxygen and zinc-oxygen complexes after gettering in the phosphorus-saturated gallium-aluminum melt. To illustrate what effect this has on minority-carrier diffusion lengths, Au/GaP Schottky solar cells were fabricated on the substrates, and the spectral response of each was examined. A marked increase in response across all wavelengths on the gettered sample indicates an increase in minority-carrier diffusion lengths. To ensure these results were not simply due to an increase in the depletion region width resulting from a change in carrier density, *C*–*V* profiling was performed and found only a small change in carrier concentration of the gettered sample.

Key words: Gettering, GaP, multijunction solar cell, photoluminescence, spectral response, capacitance–voltage

INTRODUCTION

Current state-of-the-art concentrator multijunction solar cells, comprised of three junctions, are >40% efficient.[1] While steady progress has been made to increase efficiency in these devices over the past several years, no large improvements in absolute efficiency have been made. This owes to the fact that the commonly used lattice-matched GaInP/GaAs/Ge material system is nearly optimal for a three-junction device in terms of the band gaps of each subcell. Given this, the community has begun looking into alternatives such as 4+ junction devices. To realize concentrator efficiency of 50%, these next-generation multijunction solar cells will need a top subcell with an energy gap in the vicinity of 2.4 eV.[2,3] Since there are no commercially available, 50% efficient, monolithically integrated stacks made of lattice-matched subcells having the desired band gap, some groups are investigating nonmonolithically integrated stacks using (In,Ga)N. However, owing to materials issues such as phase separation and significant defect densities, marketable cells have yet to be realized.[4,5]

Our approach has been to study GaP as the material for the top cell. While not conducive for monolithic integration into current devices due to its large lattice mismatch with the GaAs system, we envision integration by mechanically stacking the GaP cell over lower cells with separate terminals. We have extensively modeled and experimentally studied n^+/p GaP devices for concentrator cell systems. The cells used in our previous studies were fabricated by molecular-beam epitaxy (MBE) using commercial GaP substrates and achieved 2.6% AM1.5G efficiency and open-circuit voltage of 1.56 V.[6] Our simulations have shown that, for a "practical" GaP cell, AM1.5G efficiency of 12% should be possible. Modeling of our experimental

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data showed that the major losses are due to short minority-carrier diffusion lengths (MCDL) and significant surface recombination losses in the n^+ contact layer.[7] In this paper, we investigate the use of gettering to improve the MCDL in p-type GaP.

EXPERIMENTAL PROCEDURES

It is well known that, during gallium melt liquid-phase epitaxy (LPE) growth of GaAs minority-carrier devices, the liquid gallium can getter carrier-lifetime-reducing traps from bulk GaAs wafers.[8] Using this knowledge, we performed gettering experiments on a commercial zinc-doped GaP substrate ($N_A \approx 10^{18}$ cm^{-3}). The apparatus for performing the gettering experiment is shown in Fig. 1. Inside a fused quartz tube, a high-purity graphite crucible contains the melt. A high-purity graphite substrate holder attached to a quartz rod is used to hold the substrate in place while lowering into the melt. Prior to gettering, the GaP:Zn substrate was cleaned with acetone followed by isopropanol, and then soaked in HCl for 30 s to remove the native oxide. For this study, gettering was accomplished by immersing the GaP:Zn substrate into the phosphorus-saturated, 99.9999% pure gallium melt with 0.381 wt.% aluminum at 975°C for 1 h. Excess phosphorus, supplied by pieces of a GaP wafer, was used to ensure the solution was saturated, thus preventing etchback of the substrate. Forming gas (4% H_2 in N_2) was flowed at a rate of 1 L/min throughout the processing. Any melt left on the substrate or (Al,Ga)P growth that may have occurred during the gettering process was removed by an HF etch. To ensure this final etching step did not alter the underlying substrate, the same etch was performed on another piece of the as-received substrate, and all results were found to match those of the unetched, as-received substrate.

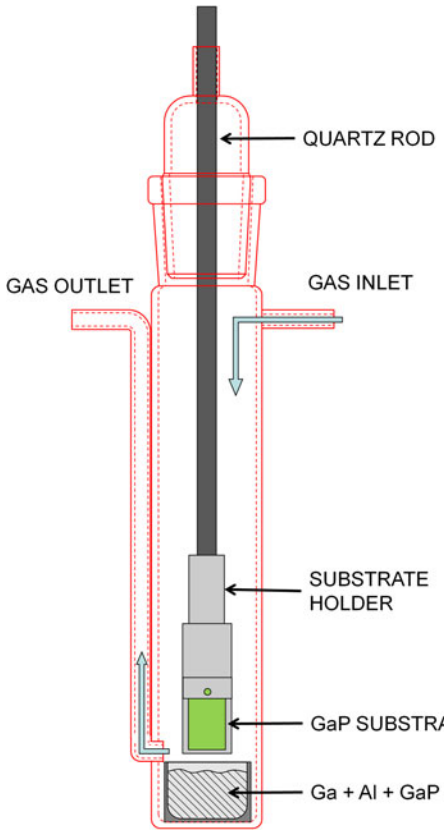

Fig. 1. Apparatus used for the GaP:Zn gettering (color figure online).

Low-temperature continuous-wave photoluminescence (cw-PL) was performed using a 325 nm HeCd laser. The samples were cooled in a liquid-helium cryostat, and both excitation and collection were performed at approximately 45° from the surface normal of the sample. The emitted signal from each sample was introduced into a spectrograph (Acton SpectraPro 300i) and eventually collected by a liquid-nitrogen-cooled charge-coupled device (CCD) array detector.

To corroborate our cw-PL findings and illustrate the effects of gettering on the MCDL, transparent Schottky solar cells and diodes were fabricated and characterized on both the as-received GaP:Zn substrate and the gettered GaP:Zn substrate. Both samples were fabricated by electron-beam deposition of 20 nm of gold on the top surface and melted indium contacts to the back. The solar cells used for spectral response measurements had area of 0.2 cm^2. Spectral response measurements were performed at zero bias. Capacitance–voltage (C–V) profiling was performed at 100 kHz on circular diodes with diameters of 200 μm and 300 μm to compare effective carrier densities near the surface.

RESULTS AND DISCUSSION

Normalized cw-PL plots taken at 4 K of the as-received and gettered substrates (Fig. 2) reveal common emission peaks at 2.20 eV, 1.82 eV, and 1.38 eV often observed in GaP:Zn.[9–11] These peaks have been identified in the literature as Zn-S pair

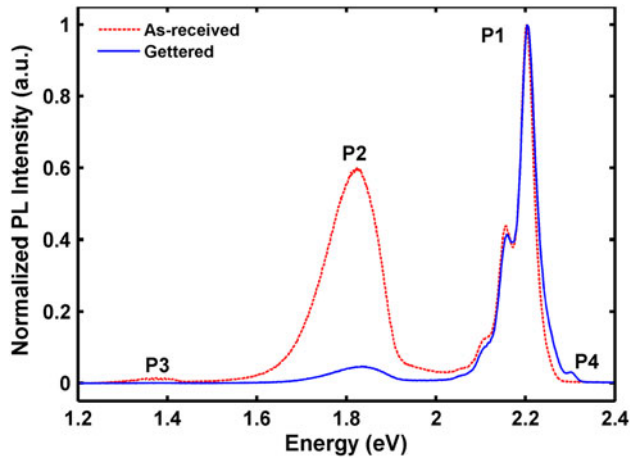

Fig. 2. Continuous-wave photoluminescence spectra of both gettered and as-received GaP:Zn samples (T = 4 K, λ_{exc} = 325 nm) (color figure online).

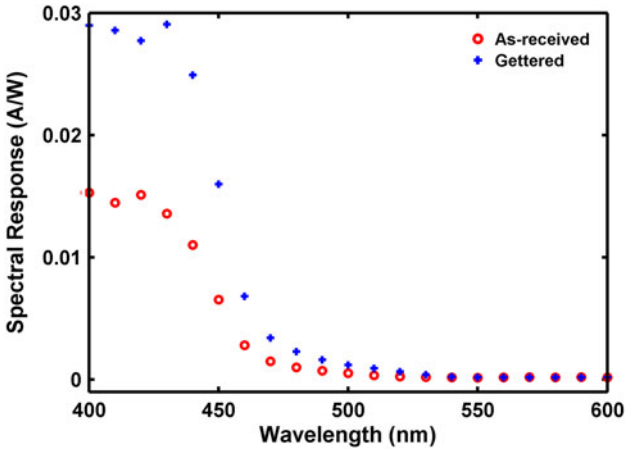

Fig. 3. Wavelength-dependent spectral response of gettered and as-received GaP:Zn samples (color figure online).

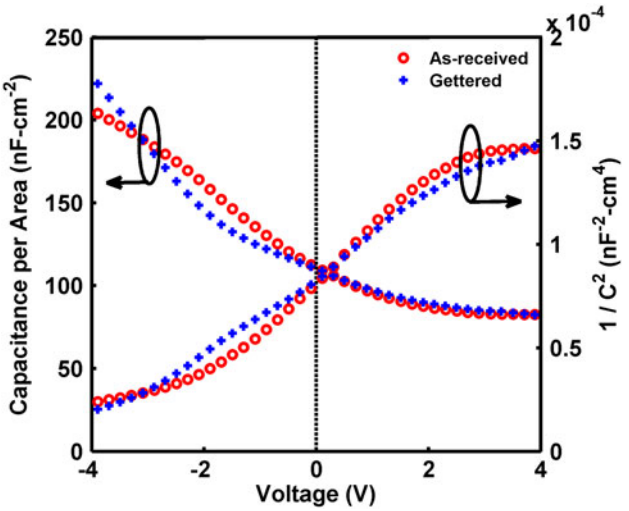

Fig. 4. 100 kHz C–V and $1/C^2$ curves of Au/GaP Schottky diodes fabricated on both gettered and as-received GaP:Zn substrates (color figure online).

recombination (P1), isoelectronic nearest-neighbor Zn-O pair recombination (P2), and widely separated Zn-O pair recombination (P3), respectively.[9–13] Additional peaks at 2.16 eV and 2.11 eV are longitudinal optical (LO) phonon replicas of the P1 peak, specifically (Zn-S)-1LO and (Zn-S)-2LO, respectively.[14] While both the as-received and gettered samples demonstrate all P1, P2, and P3 emission peaks, the ratios of the peak intensities are quite different. For the gettered sample, the relative intensities of oxygen-containing peaks (P2 and P3) to that of the Zn-S pair peak (P1) are much lower (by an order of magnitude) as compared with the as-received sample. Such results suggest that oxygen is gettered out of the substrate while soaking in the phosphorus-saturated gallium-aluminum melt. These results are comparable to those found by Demidov et al.[13] on the growth of bulk zinc-doped GaP crystals from a gallium melt with and without aluminum. More evident verification of improved substrate quality after gettering is demonstrated by the presence of a free exciton peak at 2.30 eV in GaP only observed after the gettering process (P4 in Fig. 2). This further suggests a suppression of recombination through deep levels due to a reduction in oxygen impurities.

To investigate whether any change in the MCDL results from reduction of oxygen in the gettered sample, the spectral response was taken across a range of wavelengths (Fig. 3). A near twofold improvement in spectral response was observed for the gettered sample as compared with the as-received sample (external quantum efficiency at 400 nm was 4.74% and 8.98% for the as-received and gettered samples, respectively). To ensure that this improvement was due to an increase in MCDL and not simply to a wider depletion region that may result from the removal of zinc dopants from the crystal during the gettering process, we performed C–V profiling on each sample, as shown in Fig. 4. The effective carrier density, as calculated from the slope of the $1/C^2$ curve between 0 V and 1.5 V, was 4.49×10^{17} cm^{-3} and 5.42×10^{17} cm^{-3} for the as-received and gettered samples, respectively. The small increase in carrier density within the gettered sample would cause a decrease in the depletion width, suggesting that the increase in spectral response is due entirely to an increase in the MCDL within the gettered region. As evidenced by the Zn-O-related cw-PL peak reduction after gettering, the observed increase in hole carrier density within the gettered sample is likely due to removal of oxygen donors from the substrate. However, we do not have an indication of whether we did or did not getter out some amount of zinc into the melt along with the oxygen.

These data strongly suggest that using gettered GaP:Zn substrates will greatly enhance the collection efficiency of minority carriers generated within the p-type material of a n^+/p GaP cell, assuming no additional impurities are introduced during subsequent epitaxial growth. Of particular note is the response to blue-green photons (450 nm to 500 nm), which are absorbed below the direct band edge of GaP (446 nm, 2.78 eV). In this region of the spectrum, photons generate hole–electron pairs 1 μm to 6 μm deep within GaP,[15] far from the Schottky junction. The collection of these longer-wavelength photons is nearly double in the gettered sample as compared with the as-received sample. This increased collection for the longer-wavelength photons, again, suggests an increased MCDL and correlates with the decrease in oxygen-containing deep-level cw-PL.

CONCLUSIONS

We have unambiguously shown that immersing bulk p-type GaP:Zn substrates in a phosphorus-saturated gallium-aluminum melt at 975°C for 1 h significantly reduces minority-carrier lifetime killers that are associated with oxygen. A significant

decrease in the concentration of oxygen, as indicated by low-temperature cw-PL, led to an improvement in spectral response compared with the as-received sample. C–V profiling confirms that this improvement in spectral response is not due to the change in the width of the depletion region. A small change in carrier density is suspected to be from the removal of compensating oxygen donors, though further work is required to investigate possible diffusion of zinc out of the substrate during gettering.

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