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Surface and bulk passivation of GaAs solar cell on Si substrate by H_2+PH_3 plasma

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A promising passivation method for GaAs solar cell grown on Si substrate (GaAs/Si solar cell) by phosphine-added hydrogen (PH_3/H_2) plasma exposure has been envisaged. The defect-hydrogenation and the surface-phosphidization effects of GaAs/Si solar cell are realized simultaneously by this single passivation process. Consequently, surface recombination states are reduced and the minority carrier lifetime is increased, resulting in a significant reduction in saturation current density (J_0) of the GaAs/Si *p–n* junction. High open-circuit voltage (0.93 V) and fill factor (80.9%) are obtained for the PH_3 plasma exposed GaAs/Si solar cells. As a result, the conversion efficiency is increased from 15.9% to 18.6%. This approach provides a simple and effective method to improve the photovoltaic properties of GaAs/Si solar cell. © *2000 American Institute of Physics.* [S0003-6951(00)01106-2]

In the past several years, even after putting extensive efforts on reducing the dislocation density to improve the photovoltaic properties of GaAs/Si solar cells,[1] high density of dislocation (exceeding 10^6 cm^{-2}) still persists and severely restricts practical application of this cell until now.[2] Usually, dislocation in GaAs/Si solar cells degrades both short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}), especially the open-circuit voltage.[3] It suggests that the key to improving the efficiency of GaAs/Si solar cells lies in increasing the open-circuit voltage. Pearton *et al.* reported that hydrogen (H) atoms incorporation is an effective way to passivate the electrical activity of defects and impurity states in GaAs/Si epilayer.[4] Recently, we have succeeded in increasing the conversion efficiency of GaAs/Si solar cells through hydrogen plasma exposure.[5] But exposure to H plasma also induced damages to GaAs surface, such as depletion of arsenic, which removes the beneficial effects of H incorporation.[6] It is reported that phosphorus (P) atoms effectively passivate the GaAs surface and reduce the surface state density.[7,8] Therefore, one can expect that PH_3/H_2 plasma exposure would not only hydrogenate the defect states inside GaAs/Si solar cells, but also make the surface phosphidization and suppress the plasma-induced damages.

In this letter, we report the results of PH_3/H_2 ($PH_3/H_2 = 10\%$ in ccm) plasma passivation studies performed on GaAs/Si solar cells. Both the surface phosphidization and defect hydrogenation effects of GaAs/Si solar cells were realized simultaneously in a single plasma exposure process. Very high open-circuit voltage, V_{oc} (0.93 V), and fill factor, FF (80.9%), have been obtained for such a cell and is attributed mainly to the drastic decrease in saturation current density (J_0). The converse efficiency (E_{ff}) of GaAs/Si solar cell increased from 15.9% for passivated one to 18.6% for PH_3/H_2 plasma passivated one.

The p^+-n GaAs single-junction solar cells with a 50-nm-thick AlGaAs window layer on the top were fabricated on (100) 2° off towards the [011] Si substrate using conventional atmospheric pressure metal organic chemical vapor deposition (MOCVD). The detailed growth process and the solar cell structure are described elsewhere.[9] After the growth, passivation was performed in a quartz tube at a reduced pressure (~0.1 Torr) in the ambient of H_2 or H_2+PH_3 (10%). The plasma was excited by radio-frequency (rf) wave via a copper coil encircling the quartz tube. The samples were heated up to 250 °C during the passivation process. The typical induced rf plasma power and time were 90 W and 1 h, respectively. The passivated samples were annealed in H_2 ambient at 450 °C for 10 min. After passivation, AuZn/Au and AuSb/Au electrodes were formed by vacuum evaporation for the p^+-GaAs contact layer and n^+-Si substrate, respectively. Finally, antireflection films were made of MgF_2/ZnS double layers. The total area of the GaAs solar cell was 5×5 mm^2. Four kinds of GaAs/Si solar cells were fabricated: (i) without plasma and annealing treatment (cell A); (ii) H_2 plasma exposed (cell B); (iii) PH_3/H_2 plasma exposed (cell C); and (iv) PH_3/H_2 plasma exposure followed by annealing in H_2 ambient at 450 °C (cell D).

Photoluminescence (PL) spectra were recorded at 4.2 K using a 514.5 nm Ar-ion laser (15.07 W/cm^2) as an excitation source, and a GaAs photomultiplier tube (PMT) as a detector. Time-resolved photoluminescence (TRPL) was excited by a semiconductor laser pulse ($\lambda=655$ nm, duration=50 ps) and the TRPL decay curves were measured using the photon counting method at room temperature. Auger electron spectroscopy (AES) was used to investigate the composition of both the untreated and plasma treated GaAs surfaces. Forward dark current–voltage ($I-V$) characteristics of the GaAs/Si solar cells were measured at room tem-

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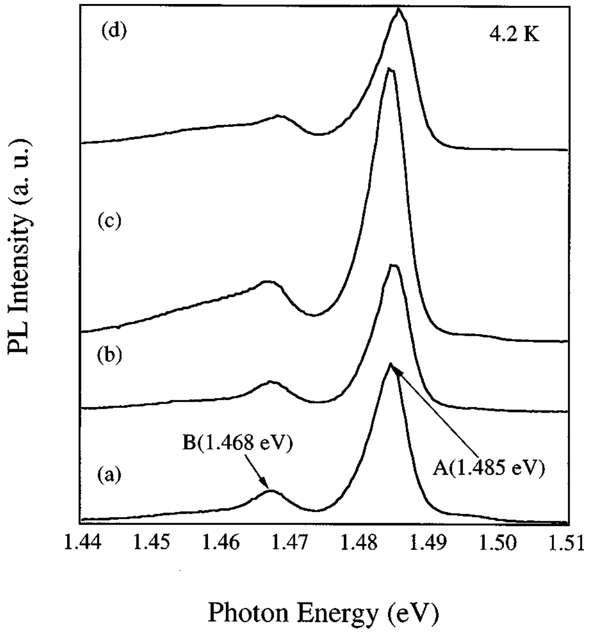

FIG. 1. PL spectra of GaAs epilayers grown on Si substrate recorded at 4.2 K; (a) as-grown, (b) H_2 plasma passivated, (c) PH_3/H_2 plasma passivated, and (d) PH_3/H_2 plasma passivated followed by annealing in H_2 ambient at 450 °C. Peaks A (1.486 eV) and B (1.468 eV) represent heavy-hole-associated free-exciton and carbon-impurity-bound exciton peaks, respectively.

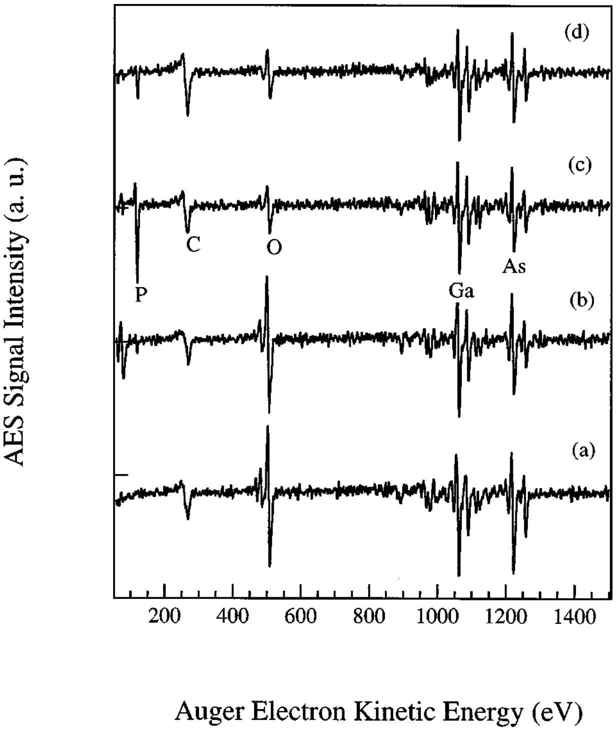

FIG. 2. Auger electron spectra for the surfaces of GaAs epilayers on Si: (a) as-grown, (b) H_2 plasma passivated, (c) PH_3/H_2 plasma passivated, and (d) PH_3/H_2 plasma passivated followed by annealing in H_2 ambient at 450 °C.

perature. The photovoltaic properties of these cells were measured under *AM*0, 1 sun conditions at 27 °C using a solar simulator. The values of the photovoltaic properties discussed are active-area values.

Figure 1 shows 4.2 K PL spectra of the unintentionally doped *n*-type GaAs (3 μm thick) epilayers on Si substrate. Two dominant peaks appear for the as-grown samples: heavy-hole-associated free-exciton peak A (1.485 eV), and carbon-bound exciton peak B (1.468 eV). Whereas the integrated PL intensity of H_2 plasma passivated sample, Fig. 1(b), shows almost no increase. PL intensity of PH_3/H_2 plasma passivated sample shows a significant increase, as shown in Fig. 1(c), compared to that of the as grown sample, Fig. 1(a). It is attributed to a decrease in surface recombination states caused by surface phosphidization due to PH_3/H_2 plasma exposure which protects the surface from oxidation.[10] However, annealing the PH_3/H_2 plasma passivated sample at 450 °C in H_2 ambient decreases the PL intensity, Fig. 1(d), which suggests that some of the plasma-induced damages are activated at this annealing temperature thereby quenching the PL efficiency.[11]

Figure 2 shows the differential Auger electron spectrum (AES) of as-deposited and plasma passivated GaAs epilayers grown on Si. Strong O signal originating from oxygen (O) impurity (at ~510 eV) can be observed for the as-deposited sample (spectrum *a*, Fig. 2), and is due to oxidation of the GaAs surface which introduces free arsenic and results in poor surface electronic properties. The H_2 plasma exposure results in a decrease in intensity of the As signal, but no decrease in intensity of the O signal can be observed, as can be seen in spectrum *b*, Fig. 2, suggesting that hydrogen terminated GaAs surface is not efficient in preventing the surface oxidation. The decrease in As may be due to the reaction of H with GaAs, which depletes the As concentration in the surface and induces some As-related deep damages. However, after PH_3/H_2 plasma exposure, phosphidization of the GaAs surface results in decrease in intensity of the As signal along with a significant decrease in O signal as well as in the appearance of a phosphorus signal at around 119 eV (spectrum *c*, Fig. 2). This can be attributed to replacement of surface As atoms by P atoms, which forms a passivating cover layer of gallium phosphide. Furthermore, P atoms

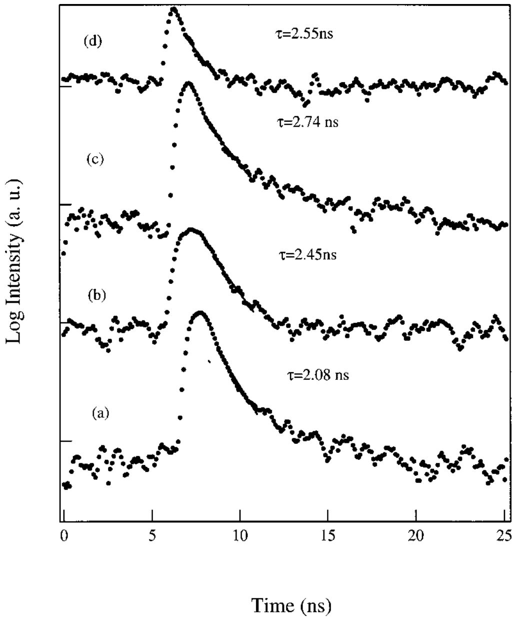

FIG. 3. Time-resolved PL decay curves of GaAs epilayers on Si, measured at room temperature; (a) as-grown, (b) H_2 plasma passivated, (c) PH_3 (PH_3/H_2= 10%) plasma passivated, and (d) PH_3 plasma passivated followed by annealing in H_2 ambient at 450 °C. The solid lines represents fitted results.

TABLE I. The photovoltaic properties of GaAs solar cells on Si under 1 sun $AM0$ illumination at 27 °C. Cell A: as-grown cell, cell B: passivated by H_2 plasma, cell C: passivated by PH_3/H_2 (PH_3/H_2= 10%) plasma, and cell D: passivated by PH_3/H_2 plasma then annealed in H_2 ambient at 450 °C.

Sample No.	J_0(A/cm^2)	J_{sc}(mA/cm^2)	$V_{oc}(V)$	FF(%)	E_{ff}(%)
cell A	1.14×10^{-9}	34.08	0.85	73.9	15.9
cell B	7.84×10^{-10}	34.46	0.88	78.6	17.7
cell C	5.72×10^{-11}	33.39	0.93	80.9	18.6
cell D	6.00×10^{-8}	34.32	0.89	78.8	17.9

were reported to fill in the plasma-induced As vacancy and suppress the generation of damages.[12] Annealing the phosphidized sample at 450 °C for 10 min in H_2 ambient reduced the intensity of P signal to some extent, but the O signal still remains weak (spectrum *d*, Fig. 2) showing high stability of the surface phosphidization.

In order to elucidate the passivation effect of nonradiative recombination centers, we also measured the minority carrier lifetime of GaAs on Si using a *n*-AlGaAs (50 nm)/GaAs (1 μm) DH structure which is least influenced by the surface condition.[13] The improvement of the slope of TRPL decay curve is due to the improvement of the bulk minority carrier lifetime of GaAs epilayer on Si. PH_3/H_2 plasma exposure [Fig. 3(c)] has been found to increase the minority carrier lifetime more effectively than H_2 plasma exposure. This can only be attributed to the passivation of AlGaAs/GaAs interfacial defects-related nonradiative recombination centers by P atoms incorporation, as the P atoms are found almost concentrated in the surface region (~50 Å) by our AES depth profiles measurement. Furthermore, this increase in the minority carrier lifetime still persists to some extent even after annealing at 450 °C, and is in good agreement with our previous results where we found that the H passivation effect of some deep defects in GaAs/Si epilayer is stable under 450 °C annealing.[14]

The typical room temperature forward dark current–voltage ($I-V$) characteristics of GaAs/Si single-junction solar cells are shown in Table I. The saturation current density J_0 of H plasma exposed cell (cell B) shows a slight decrease from 1.14×10^{-9} to 7.84×10^{-10} A/cm^2 compared to that of the as-grown cell (cell A), due to the H passivation of electrical activity of the residual defects, such as threading dislocations.[15] For PH_3/H_2 plasma passivated cell (cell C), a lowest value of 5.72×10^{-11} A/cm^2 of J_0 is obtained. This further decrease in J_0 by addition of PH_3 to H_2 plasma can only be attributed to the surface phosphidization effects by P atoms incorporation. Annealing the phosphidized cell (cell D) at 450 °C makes it more leaky due to the reactivation of plasma-induced damages, as discussed before. It is very clear that both H and P atoms play an important role in the passivation process by PH_3/H_2 plasma exposure.

Table I also shows the photovoltaic properties of the above four cells (cells A–D) measured under $AM0$, 1 sun, 27 °C conditions. Compared with the untreated cell A, the H_2 plasma passivated cell B shows an increase in both the short-circuit current density, J_{sc}, from 34.08 to 34.46 mA/cm^2, and open-circuit, V_{oc}, from 0.85 to 0.88 V. As a result, the conversion efficiency, E_{ff}, is increased from 15.9% to 17.6%. For the PH_3/H_2 plasma passivated cell C, very high V_{oc} (0.93 eV) and FF (80.9%) are obtained due to the very low value of J_0, leading to further improvement in E_{ff} (18.6%). However, J_{sc} of the PH_3/H_2 passivated cell is also suppressed to some degree, which may be due to the formation of III–V/P compound thin layer over the AlGaAs window layer which causes slightly more photons to be absorbed in the window layer and reduces J_{sc}.[16] In order to test the thermal stability, the PH_3/H_2 passivated cell was annealed in H_2 ambient at 450 °C. The annealed cell (cell D) still showed a very high E_{ff} (17.9%), suggesting that PH_3/H_2 plasma passivation is very useful for practical application, as the process temperature of device fabrication is usually below 450 °C.

In summary, using PH_3/H_2 plasma passivation, the surface phosphidization and bulk hydrogenation effects of GaAs/Si solar cells are realized simultaneously. Consequently, the saturation current density of the passivated cell is significantly decreased due to reduction of surface recombination velocity and increase of minority carrier lifetime, resulting in very high V_{oc} (0.93 V) and FF (80.9) for GaAs/Si solar cell. The E_{ff} is improved from 15.8% to 18.6% with this single passivation process. Thus PH_3/H_2 plasma passivation opens an interesting and promising way to improve the characteristics of GaAs on Si devices.

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