PH_3/H_2 plasma passivation of metal-organic chemical vapor deposition grown GaAs on Si

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Effects of PH_3/H_2 (PH_3/H_2=10%) plasma passivation of GaAs grown on Si substrate have been investigated in detail. It is observed that both the surface phosphidization and defect hydrogenation can be realized simultaneously with a reduced plasma-induced damage. The optical and electrical properties of GaAs on Si are effectively improved by PH_3/H_2 plasma exposure due to the passivation of bulk and surface defects-related nonradiative recombination centers by incorporation of hydrogen (H) and phosphorous (P) atoms. As a result, the PH_3/H_2 plasma exposed GaAs Schottky diodes on Si show an increase in the reverse breakdown voltage by a factor of about 1.6, and the as-passivated GaAs solar cell grown on Si shows an increase in the conversion efficiency from 15.9% to 18.6% compared to that of the as-grown samples. The passivated GaAs devices on Si show outstanding thermal stability, which is probably due to the active participation of both H and P atoms in the PH_3/H_2 plasma passivation process.
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I. INTRODUCTION

It is well known that high density of defects, such as threading dislocations ($\sim 10^6 cm^{-2}$), in GaAs grown on Si substrates (GaAs/Si) severely restricts this heteroepitaxial technology for its widespread application. These defects act as nonradiative recombination centers, which prevent the long life operation of the laser device and seriously degrade the photovoltaic properties of GaAs/Si solar cells.[1] Much effort has been made to reduce the dislocations in GaAs/Si epilayers, but with limited success due to the intrinsic mismatches between the GaAs epilayer and Si substrate, such as the lattice mismatch of around 4.1% and thermal expansion coefficient mismatch of around 60%. There has recently been a renewed interest in the development of hydrogen (H) plasma passivation method for GaAs/Si, which have led to improved optical and electrical properties.[2] But due to the high reactivity of atomic hydrogen with the surface of III–V compounds, exposure to H plasma also induces etching and damages in the near surface region.[3] Therefore, there is a need to minimize these negative influences of plasma-induced damages.

Phosphidization of the GaAs surface by phosphorus (P) atom incorporation has been extensively investigated.[4] Via an As/P exchange mechanism, a passivating cover layer of gallium phosphide (GaP) is expected to form, suggested which protects the GaAs surface from oxidation and reduces the surface state density.[5] Some improvement in the electrical properties of GaAs Schottky diodes has been reported.[6] The P atoms are substituted for As-related defect centers and suppress the generation of EL2 centers near the surface.[7] Consequently, the presence of atomic P in the plasma is effective in suppressing the generation of plasma-induced damages.

In the present study, metal-organic chemical vapor deposition (MOCVD) grown GaAs/Si epilayers are exposed to PH_3/H_2 (PH_3/H_2= 10%) plasma which involves both atomic P and H. Therefore, along with the hydrogenation of the shallow levels and defect-related deep levels in GaAs/Si by H incorporation, the surface phosphidization is also realized by PH_3/H_2 plasma exposure. The passivation effects of PH_3/H_2 plasma exposure on the optical and electrical properties of GaAs/Si epilayer are characterized by electrochemical capacitance–voltage (C–V), photoluminescence (PL), time-resolved photoluminescence (TRP), and deep-level transient spectroscopy (DLTS) method. An improved room temperature PL efficiency and minority carrier lifetime are obtained due to the passivation of the nonradiative recombination centers, which is very consistent with the DLTS measurement results. In addition, the influences of the PH_3/H_2 plasma exposure on the GaAs/Si Schottky diodes and solar cells are also investigated. The PH_3/H_2 plasma exposed GaAs/Si Schottky diodes show increased reverse breakdown voltage from 8 to 13 V. For the GaAs/Si solar cells, a significant increase in open circuit voltage is realized only by

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PH_3/H_2 plasma passivation. As a result, the conversion efficiency is improved. Moreover, the annealing effect on PH_3/H_2 plasma passivated GaAs/Si is analyzed. It is found that the passivated effects are still stable under the 450 °C annealing in H_2 ambient, and thus very useful for technological process.

II. EXPERIMENT

The epitaxial growth was performed by atmospheric-pressure metal-organic chemical vapor deposition (MOCVD) on n^+-Si substrate, oriented 2° off (100) toward [011], using the two-step growth technique. The source materials for Ga, Al, and As were trimethylgallium (TMG), trimethylallumi-num (TMA), and arsine (AsH_3), respectively. The Si substrate was etched in an aqueous solution of HF, and thermally cleaned at 1000 °C for 10 min in a hydrogen ambient to remove the surface native oxide on the substrate. First a 10-nm-thick GaAs buffer layer was grown at 400 °C. Then a 3-μm-thick unintentionally doped GaAs top layer was grown at 750 °C. An AlGaAs (50 nm)/GaAs double heterostructure (DH) with a thickness of 1 μm was also prepared for the time-resolved photoluminescence (TRP) measurement.

The passivation was carried out in a quartz tube through which molecular hydrogen was pumped at a reduced pressure (0.1 Torr). The PH_3/H_2 plasma was excited by radio-frequency (13.56 MHz) power via a copper coil encircling the quartz tube. The input power used for the hydrogen plasma was 90 W. Typical plasma exposure conditions were 90 min at 250–300 °C. In order to investigate the stability of passivation effects, a postplasma-exposure annealing was carried out in H_2 ambient at 450 °C for 10 min.

Carrier concentration profiles were obtained by electrochemical capacitance voltage measurement using a Polaron model PN4200 system. Auger electron spectroscopy (AES) was used to investigate the PH_3/H_2 plasma passivated GaAs surface with a 5 keV Ar-ion beam. PL spectra were recorded at room temperature (RT) using a 514.5 nm Ar-ion laser as an excitation source, and a GaAs photomultiplier tube (PMT) as a detector. Time-resolved photoluminescence (TRP) was excited by the semiconductor laser pulse ($\lambda = 655$ nm) and the TRP decay curves were recorded by a multichannel analyzer using the photon counting method at room temperature. For the GaAs/Si Schottky diodes, gold (Au) Schottky contacts were made on GaAs, with AuSb/Au ohmic contacts on the back side of the Si substrate after the passivation and annealing treatment. Forward current–voltage (I–V) characteristics of the Au–GaAs/Si Schottky diodes are measured at room temperature in darkness. DLTS measurements were carried out using an automated (HORIBA DA 1500) system at temperatures ranging from 100 to 400 K.

A p^+-n GaAs single-junction solar cell was fabricated on n^+-Si substrate. The two-step growth method and *in situ* thermal cycle annealing (TCA) were adopted. After the growth of a 1.5-μm-thick GaAs buffer layer at 750 °C, the thermal cycle annealing (TCA) from 300 to 900 °C was carried out 5 times to improve the quality of the GaAs/Si film. Then the p^+-n GaAs single junction solar cells were grown at 750 °C followed by the growth of 50 nm $p^+-Al_{0.8}Ga_{0.2}As$ window layer of 800 °C. After the growth process, the epilayers were transferred into the plasma reactor to complete the PH_3/H_2 plasma exposure. Then AuZn/Au and AuSb/Au electrodes were formed by vacuum evaporating for the p^+-GaAs layer and n^+-Si substrate, respectively. MgF_2/ZnS double layer antireflection films were deposited. The area of the solar cell was 5×5 mm^2. The schematic cross-section structure of these solar cells is shown in Fig. 1. The photovoltaic properties of these cells were measured under AMO, 1 sun conditions at 27 °C using a solar simulator. The values of the photovoltaic properties discussed are active-area values.

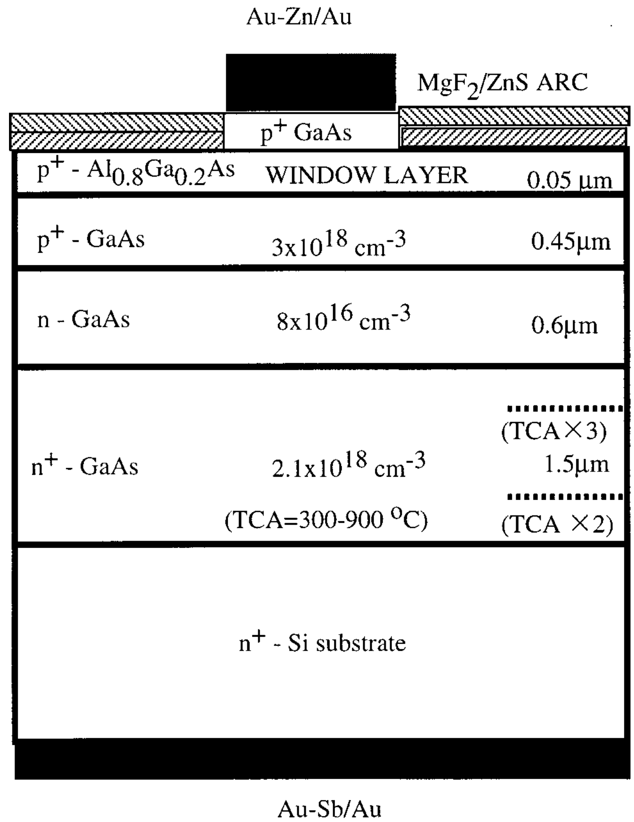

FIG. 1. The schematic cross-section structure of GaAs solar cells grown on Si substrate by MOCVD.

III. RESULTS AND DISCUSSION

A. Capacitance–voltage profiling studies

The MOCVD-grown unintentionally doped GaAs epilayer on Si substrate usually has a high background free electron concentration due to the involved shallow defects and/or shallow impurity levels. It is very difficult to grow high resistivity undoped GaAs epilayers on Si using the MOCVD technique. This becomes a crucial problem in the fabrication of GaAs metal–semiconductor field-effect transistors (MESFETs) and high electron mobility transistors (HEMTs), because the pinch-off characteristics of GaAs MESFETs and HEMTs grown on Si by MOCVD are often degraded by high carrier concentration in undoped layers. As a large number of

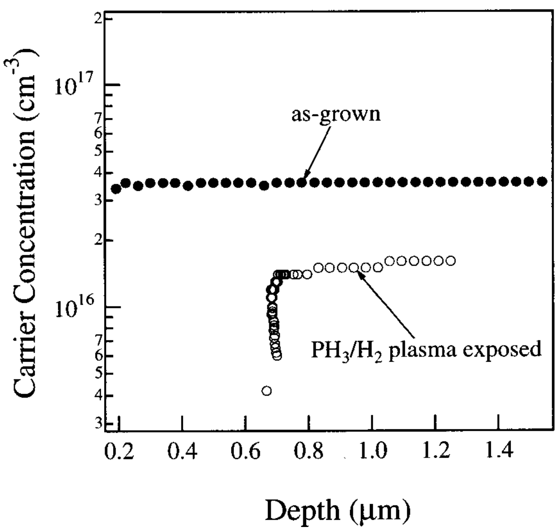

FIG. 2. Free electron concentration depth profiles for as-grown and PH_3/H_2 plasma exposed MOCVD-grown unintentionally doped *n*–GaAs/Si epilayers.

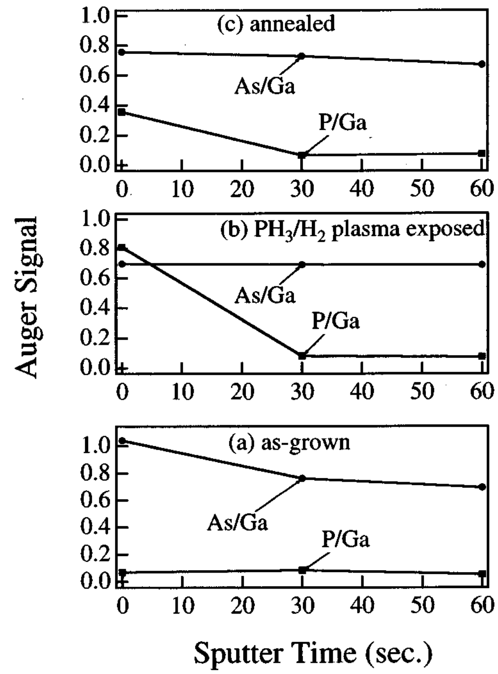

FIG. 3. Auger signals of As/Ga and P/Ga as a function of sputter time for the GaAs/Si epilayers: (A) as grown, (B) PH_3/H_2 plasma exposed, (C) PH_3/H_2 plasma exposed then annealed in H_2 ambient at 450 °C for 10 min.

H atoms are involved in the PH_3/H_2 plasma, the passivation of shallow defects in unintentionally doped GaAs/Si by H atoms is expected.

Figure 2 shows free electron depth profiles from the unintentionally doped MOCVD-grown GaA/Si, obtained from electrochemical C–V measurement before and after PH_3/H_2 plasma exposure. It can be seen that free electron concentration decreases dramatically after the passivation process from 3.6×10^{16} cm^{-3} for the as-grown sample to 1.5×10^{16} cm^{-3} for the PH_3/H_2 plasma exposed sample at the depth of 1 μm from the surface. However, the free electron concentration is almost restored after annealing at 450 °C for 10 min in H_2 ambient. These results strongly suggest that the PH_3/H_2 plasma exposure can effectively passivate the shallow defects and impurity levels in GaAs grown on Si substrate by H atoms incorporation.

B. Auger electron spectroscopy studies

The compositional structure along the depth of the film was profiled by measuring the Ga-Auger peak (1070 eV), As-Auger peak (1228 eV), and P-Auger peak (119 eV) intensities. Figure 3 shows the As/Ga and P/Ga Auger signals ratios as a function of sputter time for the GaAs on Si before, after PH_3/H_2 plasma exposure and after annealing the PH_3/H_2 plasma exposure at 450 °C for 10 min in H_2 ambient. It can be clearly seen that the Auger signal of P atoms significantly increases whereas that of As atoms decreases after the PH_3/H_2 plasma exposure. This can be attributed to replacement of surface As atoms by P atoms, which forms a passivating cover layer of gallium phosphide. Group III–V phosphides are characterized by lower oxidation rate and lower surface states density than the arsenides. However, after removing about 50 Å of the material, which corresponds to 30 s, sputtering time, the Auger intensity decreases to its reference value. This means that PH_3/H_2 plasma exposure phosphidizes only the GaAs surface or the region located very close to the surface. After annealing the phosphidized sample at 450 °C for 10 min in H_2 ambient, the intensity of P signal still partly remains, and shows that surface phosphidization was still stable even under this annealing treatment.

C. Photoluminescence studies

Figure 4 shows the room-temperature PL spectra measured for GaAs/Si before, and after PH_3/H_2 plasma exposure. The room-temperature PL peak is identified as a conduction–band to valence–band transition, since the exciton- and shallow-donor-related luminescences were ther-

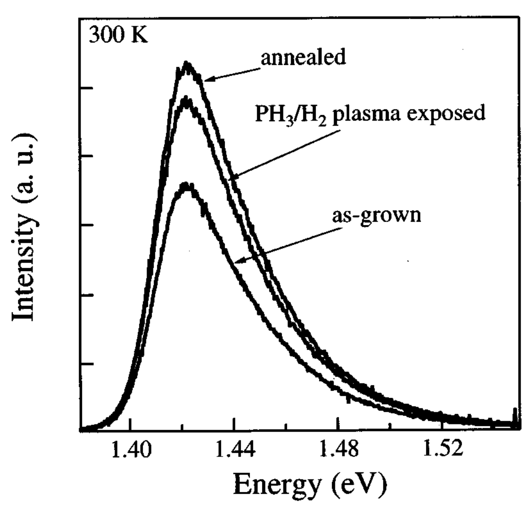

FIG. 4. The room temperature PL spectra of GaAs/Si epilayers for as-grown, PH_3/H_2 plasma exposed, and PH_3/H_2 plasma exposed then annealed in H_2 ambient at 450 °C for 10 min samples.

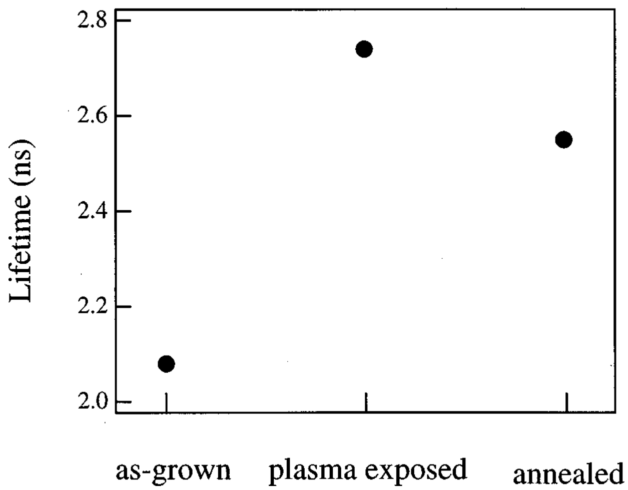

FIG. 5. Minority carrier lifetime obtained from AlGaAs/GaAs DH structures for as-grown, PH_3/H_2 plasma exposed, and PH_3/H_2 plasma exposed then annealed in H_2 ambient at 450 °C for 10 min samples.

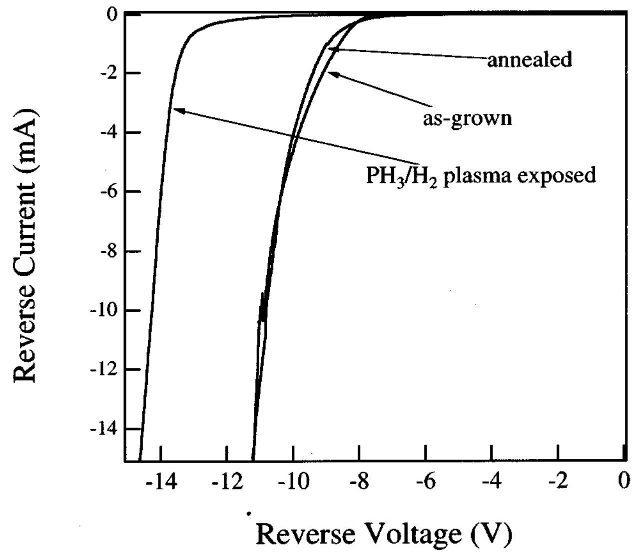

FIG. 6. The reverse current voltage characteristics of Au–GaAs/Si Schottky diodes for as-grown, PH_3/H_2 plasma exposed, and PH_3/H_2 plasma exposed then annealed in H_2 ambient at 450 °C for 10 min diodes.

mally quenched at room temperature and the band-to-band (BB) recombination dominates the spectra, which is frequently used to characterize the quantum efficiency of the samples. It can be seen that the PH_3/H_2 plasma exposure effectively increases the PL efficiency of the GaAs/Si and decreases the full width at half maximum (FWHM) from 42.4 to 41.1 meV compared to that of as-grown sample, may be due to the P atoms incorporation into the surface region, which decreases the surface-state density and lowers the surface recombination velocity. But the increase in the PL intensity after plasma exposure is only marginal, considering the fact that the H_2 plasma passivation decreased the PL intensity, it is thought that some plasma-induced damages still exist during the PH_3/H_2 plasma process and quench the PL intensity. After annealing the PH_3/H_2 plasma exposed sample at 450 °C for 10 min, the intensity is further increased which may be due to the recovery of the electrical activity of the donors (Si). It also suggests that the surface phosphidization effects are thermally stable.

For optoelectronic devices, e.g., lasers on solar cells, the minority carrier recombination plays a major role in determining device performance. The PL decay curves of the AlGaAs/GaAs DH structure grown on Si substrate were measured at room temperature. Neglecting the AlGaAs/GaAs interface recombination, the lifetime of minority carrier can be calculated by the slope of the decay curve,[8] and the calculated results are shown in Fig. 5. As shown in Fig. 5, after the PH_3/H_2 plasma exposure, the minority lifetime increases from 2.08 to 2.74 ns and decreases to 2.55 ns for the sample annealed at 450 °C in H_2 ambient after passivation. This result shows a strong improvement of minority carrier lifetime of GaAs/Si by PH_3/H_2 plasma exposure, which exists to some extent even after the annealing process. The decrease in minority lifetime after annealing may be due to the partial removal of H passivation effects and restoration of the free carrier concentration. As the P atoms are found to be concentrated in the surface region, the increase in minority carrier lifetime can be mainly contributed to the passivation of the defect-related nonradiative recombination centers in GaAs/Si by H atoms incorporation during PH_3/H_2 plasma exposure. This is also corroborated by the fact that annealing treatment increases the room temperature PL intensity and decreases the minority carrier lifetime, compared with that of the as-passivated samples.

D. Schottky diode studies

For the GaAs/Si Schottky diode, its performance is degenerated by the presence of high reverse bias leakage currents and premature breakdown of the diodes, whose origin is related to the high defect, such as threading dislocation density in the material.[3] As shown in Fig. 6, the PH_3/H_2 plasma exposure effectively increases the reverse currents breakdown voltage (V_{br}) of Au–GaAs/Si Schottky diode from 8.6 to 13.3 V compared to that of as-grown diode. V_{br} is defined as the voltage at which the reverse leakage current is 1 mA. This improvement in V_{br} can be attributed to the passivation of the dislocation-related deep defects by H incorporation. As shown in Fig. 6, even after the annealing treatment, the PH_3/H_2 plasma exposed diodes still show slightly good reverse current–voltage (I–V) characteristics compared to that of as-grown samples. For the H_2 plasma exposure, although the as-exposed diodes shows an increase in V_{br}, the annealing treatment seriously degraded the diodes due to the plasma-induced damages. The presence of P atoms in H_2 plasma process effectively suppress the plasma-induced damages.

Figure 7 shows the DLTS spectra obtained from Au–GaAs/Si Schottky diodes before and after PH_3 plasma exposure. The DLTS spectrum for as-grown sample represents three main electron traps EL2 (0.73 eV), ED1 (0.44 eV), and EL6 (0.32 eV). The EL6 deep level is very similar to the T3 level described by Sakai and Ikoma, which could be due to lattice defect or donor-Ga-vacancy complex.[9] The ED1 level is report by Soga *et al.*, which they attributed to Si-dislocation complex which has a distributed energy centered

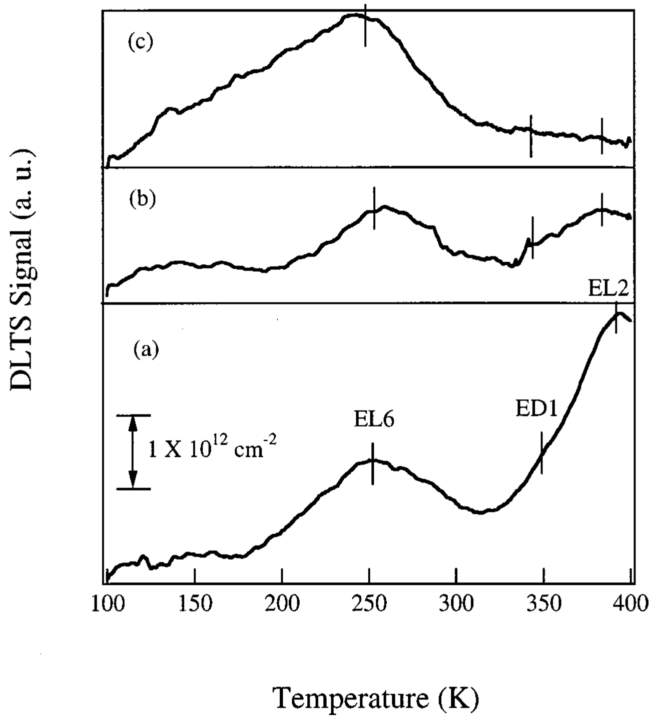

FIG. 7. Deep level spectra for (A) as-grown, (B) PH_3/H_2 plasma exposed, and (C) PH_3/H_2 plasma exposed then annealed in H_2 ambient at 450 °C for 10 min Au–GaAs/Si Schottky diodes. ED1 level is described as the dislocation-related deep levels in GaAs on Si.

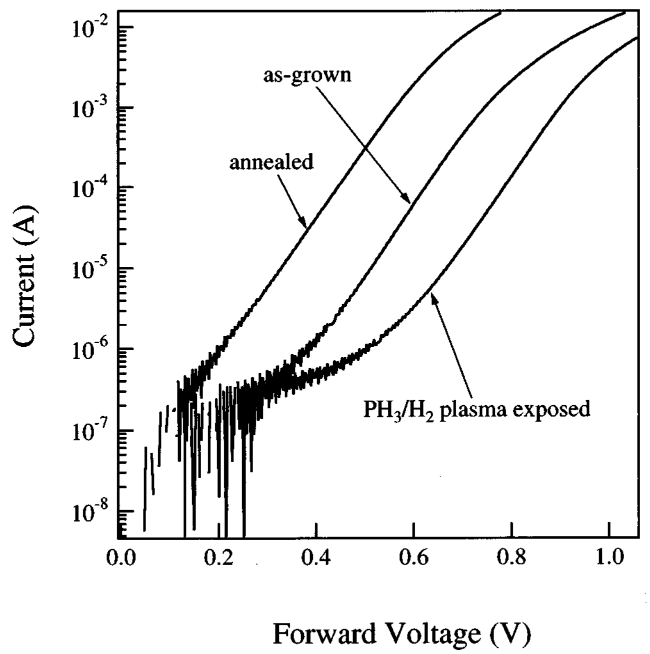

FIG. 8. Dark current–voltage characteristics of GaAs/Si single-junction solar cells measured for as-grown, PH_3/H_2 plasma exposed, and PH_3/H_2 plasma exposed then annealed in H_2 ambient at 450 °C for 10 min cells.

at around 0.44 eV.[10] A comparison with our previous results shows that PH_3/H_2 plasma exposure effectively reduces most of deep level concentration, just as the H_2 plasma exposure does.[11] Furthermore, PH_3/H_2 plasma exposure is found to be more effective in passivating the EL2 centers, which may be due to isolated As_{Ga} or As_{Ga}-related complexes, P atoms are substituted for As-related defect centers and suppress generation of plasma-induced defects. After the annealing treatment at 450 °C, the passivation effects of EL2 centers still remain. This gives a direct proof of the thermal stability of the PH_3/H_2 plasma passivation effects.

E. Solar cell studies

The GaAs/Si solar cells show degradation compared to GaAs/GaAs in short-circuit current density (J_{sc}), and particularly in open-circuit voltage (V_{oc}). It suggests that the key to improving the efficiency of GaAs/Si solar cells lies in increasing the open-circuit voltage. From our previous results of H_2 plasma exposure effects on GaAs/Si solar cells, we found an increase in V_{oc} for the as-exposed cells, however, the shunt resistance degraded due to the plasma-induced damages.[12]

The typical room temperature forward dark current–voltage (I–V) characteristics of GaAs/Si single-junction solar cells are shown in Fig. 8. The saturation current density J_0 of PH_3/H_2 plasma exposed cell shows decreases from 1.14×10^{-9} to 5.72×10^{-11} A/cm^2 compared to that of the as-grown cell, due to the passivation of electrical activity of the residual defects, such as threading dislocations. Annealing the phosphidized cell at 450 °C makes it more leaky ($J_0=6.00\times10^{-8}$ A/cm^2), this may be due to the annealing treatment which partly remove the passivation effects and reactivate some of plasma-induced damages. 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.

Figure 9 shows the photovoltaic current density-voltage characteristics of GaAs/Si solar cell before and after PH_3/H_2 plasma exposure measured under AM0, 1 sun, 27 °C condi-

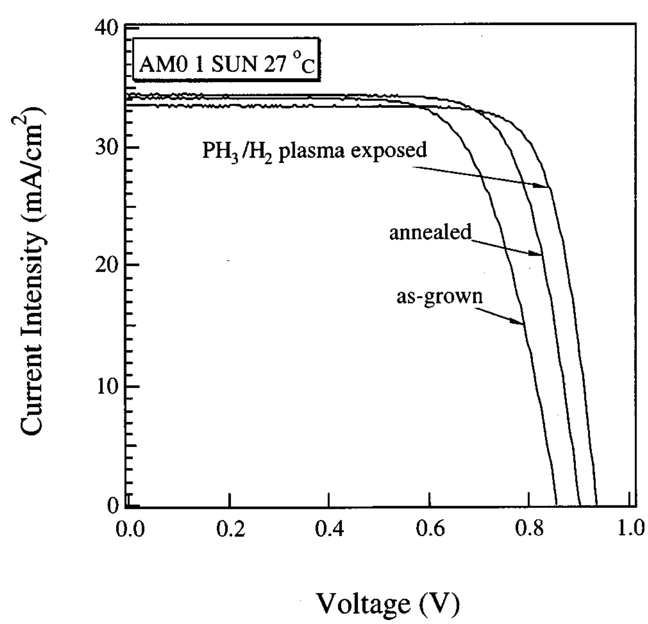

FIG. 9. Photovoltaic current density-voltage characteristics of GaAs/Si single-junction solar cells measured under AM0, 1 sun, 27 °C condition for as-grown. PH_3/H_2 plasma exposed, and PH_3/H_2 plasma exposed then annealed in H_2 ambient at 450 °C for 10 min cells.

tions. For the PH_3/H_2 plasma passivated cell, high V_{oc} (0.93 V) and fill factor FF (80.9%) are obtained compared to that of the as-grown cell (0.85 V and 73.9%, respectively). As a result, the conversion efficiency (E_{ff}) is increased from 15.9% to 18.6%. But the J_{sc} of the PH_3/H_2 exposed cell is suppressed from 34.08 to 33.39 mA/cm^2. This could be due to the formation of GaP thin layer over the AlGaAs window layer which leads to slightly more photons being absorbed in the window layer and reduces the J_{sc}. After annealing the PH_3/H_2 exposed cell at 450 °C, the J_{sc} is increased to some extent (34.32 mA/cm^2) and the V_{oc} (0.89 V) and E_{ff} (17.9%) are still larger than that of the as-grown cell. This can be attributed to the still partly remained passivation effects of P and H atoms after annealing treatment. This suggests that the PH_3/H_2 plasma exposed GaAs/Si solar cells have improved photovoltaic characteristics and a superior thermal stability.

IV. CONCLUSION

The PH_3/H_2 plasma passivation effects on MOCVD-grown GaAs/Si have been studied in detail. It is found that both the surface phosphidization and defect hydrogenation can be realized simultaneously. As a result, the optical and electrical properties of GaAs/Si are effectively improved. The PH_3/H_2 plasma exposure effects on GaAs/Si devices have also been investigated. Due to the defect passivation effects obtained by H and P atoms incorporation, reverse breakdown voltage of Au–GaAs/Si Schottky diodes increased by a factor of about 1.6, and conversion efficiency of the GaAs/Si solar cell increased by 2.7% from 15.9% to 18.6% with a large increase in open circuit voltage. Furthermore, the improved device characteristics still partly remained under the 450 °C annealing treatment. This shows that the presence of P atoms in H plasma process is effective in suppressing the plasma-induced As-related damages. The thermal stability of the PH_3/H_2 plasma exposed GaAs/Si devices opens a renewed possibility to apply the plasma passivation techniques for practical application.

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