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Passivation of dislocations in GaAs grown on Si substrates by phosphine (PH_3) plasma exposure

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The phosphidization effect on dislocations in GaAs grown on Si substrate (GaAs/Si) has been investigated. It was found that the high density of dislocations in GaAs/Si heteroepitaxial layers largely enhanced the diffusion of phosphorus (P) atoms during the phosphine (PH_3) plasma exposure. The incorporated P atoms strongly passivated the electrical states of residual dislocations in GaAs/Si solar cell. As a result, the PH_3 plasma exposure largely increased the open circuit voltage (V_{oc}) and the efficiency of GaAs/Si solar cell. *© 2001 American Institute of Physics.* [DOI: 10.1063/1.1376433]

There has recently been a great deal of reports on phosphidization of the surface of GaAs electronic and optoelectronic devices by formation of a passivating cover layer of gallium phosphide.[1–3] More recently, improvement in the electrical properties of GaAs metal semiconductor field effect transistors has been reported by the treatment in a phosphine (PH_3) plasma.[4] The P atoms are reported to be substituted for As-related defect centers and suppress the generation of EL2 centers near the surface.[5] However, the phosphidization of a dislocation in a GaAs layer has not been reported yet. If the dislocation can be electrically passivated by the phosphidization, heteroepitaxially grown GaAs on dissimilar substrates can be used for the practical application, such as solar cells, lasers, etc. For GaAs grown on Si substrates (GaAs/Si), not only the passivation of the surface defects but also the passivation of the bulk defects [in particular the threading dislocations $(\sim 10^6\ \mathrm{cm}^{-2})$, which result from the 4% lattice constant difference between GaAs and Si] are very important to improve the performance of GaAs/Si devices. Recently, we have reported the improvement of GaAs solar cell efficiency by phosphidization.[6] However, the mechanism of the improvement has not been clarified yet. In this letter, the phosphidization effect on dislocation in GaAs/Si by PH_3 plasma exposure was investigated, especially along the depth direction.

The epitaxial structure was grown by conventional atmospheric pressure metalorganic chemical vapor deposition (MOCVD) on (100) 2° off towards the [011] Si substrate. The total thickness of the epitaxially grown GaAs solar cell on Si substrate was about 2.5 μm. The detailed growth process and the GaAs/Si solar cell structure are described elsewhere.[6,7] The growth temperature is 750 °C, and the thermal cycle annealing was performed five times during the growth in order to reduce the dislocation density with a maximum temperature of 950 °C. After the growth, the plasma exposure was performed in a radio frequency (rf) (13.56 MHz) plasma chamber in an ambient of PH_3 diluted at 10% with hydrogen (PH_3 plasma). The induced power used for the plasma was 90 W with typical plasma exposure conditions of 1 h, 250 °C, and 0.1 Torr. The PH_3 plasma treatment was also performed for a GaAs substrate (dislocation density is lower than $10^4\ \mathrm{cm}^{-2}$) for comparison. The depth profiles of P atoms diffused into the samples during plasma treatment were analyzed by Auger electron spectroscopy (AES). The density of dislocation-related recombination centers in the GaAs/Si solar cell were measured by dark spot density (DSD) of electron beam induced current (EBIC) image. The acceleration voltage for the electron beam induced on the electrode of the GaAs/Si solar cell was 20 kV. The photovoltaic properties of these cells were measured under AM0, 1 sun conditions at 27 °C using a solar simulator. The values of the photovoltaic properties discussed are active-area values.

When GaAs solar cells are grown on Si substrates, a large number of dislocations which act as recombination centers and degrade the solar cell efficiency are generated. A direct determination of the density of dislocations is possible with the EBIC technique. In this case, electron–hole pairs are generated by an electron beam in a scanning electron microscope (SEM), then separated by a built-in electrical field in the *pn* junction just like the photogenerated electron–hole pairs in the solar cell. The resulting current is amplified and used to modulate the signal of the SEM monitor. The collected current is reduced at defects because of the locally enhanced carrier recombination, therefore, the defects show up as a dark feature in the SEM image.[8] It is reported that the dark spots correspond to dislocations in the case of GaAs on

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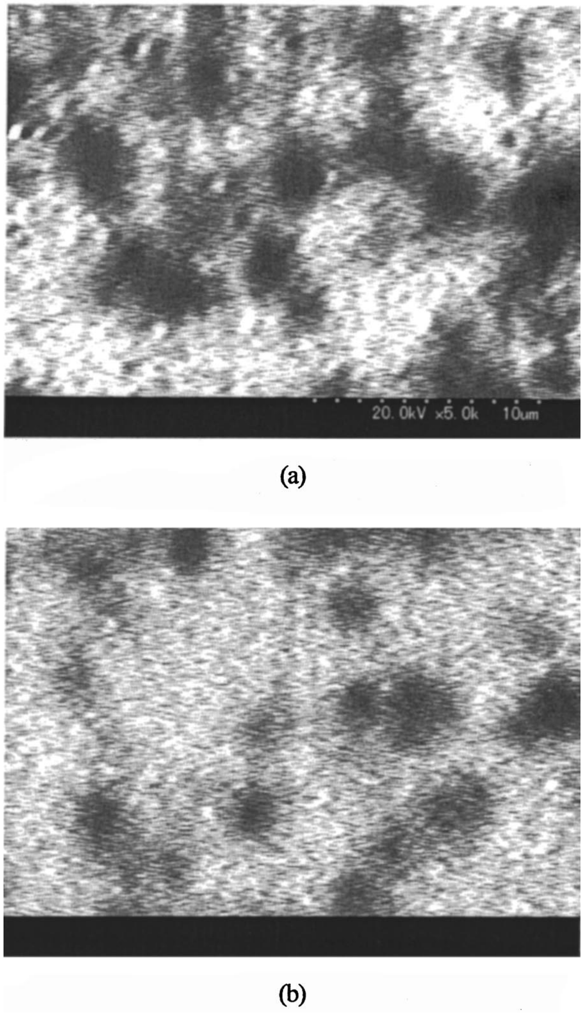

FIG. 1. Typical EBIC image of GaAs solar cells grown on Si substrates before (a) and after (b) PH_3 plasma exposure.

Si.[9] Figure 1 shows the EBIC image of GaAs/Si solar cells before and after PH_3 plasma exposure. We measured the DSD to evaluate the dislocation density in the *pn* junction region of GaAs/Si solar cells. For the PH_3 plasma exposed solar cell, the dark spot density was remarkably reduced to about $3\times10^6\,cm^{-2}$ compared to that of the unexposed cell ($\sim7\times10^6\,cm^{-2}$). The passivation effect of dislocations by hydrogen atoms during the plasma exposure can be ignored, because the DSD was not reduced by the hydrogen plasma exposure without PH_3 gas under similar conditions. It means that the significant reduction of dislocation density can be achieved only when the PH_3 plasma was used.

There are several possible reasons for the reduction of dislocation density by PH_3 plasma treatment. One is the thermal annealing effect. But, the temperature of the sample during the PH_3 plasma treatment is 250 °C, which is much lower than the growth temperature of GaAs: 750 °C. It has been reported that the dislocation density can be reduced when the annealing temperature is comparable or higher than the growth temperature.[10] Also in our experiment, the dislocation density reduction was not observed by the annealing at 250 °C in hydrogen plasma exposure. Therefore, the dislocation reduction by annealing effect is ruled out. Hydrogen effect is also ruled out because the dislocation density was not decreased only by the hydrogen gas, as mentioned above. The plasma effect is also ruled out because plasma-induced ions create damage in the GaAs layer on Si substrate, but does not improve the crystal quality. Therefore, for the mechanism of dislocation reduction, the passivation of dislocations by P atoms can be considered. In order to evaluate the incorporation of P atoms in the dislocations of the GaAs layers, the samples were evaluated by AES.

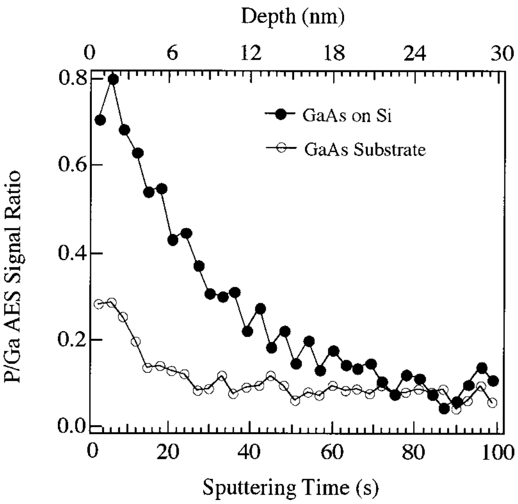

FIG. 2. Auger signals of P/Ga as a function of sputter time and depth for the GaAs/Si epilayer and GaAs substrate after PH_3 plasma exposure.

The incorporation of P atoms along the depth of the GaAs/Si epilayer was profiled by measuring the Ga-Auger peak (1070 eV) and P-Auger peak (119 eV) intensities. Figure 2 shows the P/Ga Auger signal ratios as a function of sputter time and depth for the GaAs/Si epilayer and GaAs substrate after PH_3 plasma exposure. The observation of an AES signal for P atoms in the deeper region was limited by the detection sensitivity of the AES measurement. The flat portion of the signal of P atoms in Fig. 2 was due to detection limit of AES. A high concentration of P atoms was detected up to a sputtering time of 80 s (which corresponds to a depth of about 24 nm removed by sputtering) for the highly dislocated GaAs/Si epilayer after PH_3 plasma exposure. Compared with that diffused into the surface region of the GaAs/Si epilayer, it is clearly seen that both the amount and the depth of P atoms diffused into nondislocated GaAs substrate under the same plasma exposure procedure was much smaller. Although there are no reports about the relationship between P atoms diffusion and the density of dislocation in GaAs/Si epilayer, the enhanced diffusion of P atoms into the GaAs/Si epilayer during the PH_3 plasma exposure would be explained by a dislocation-related pipe diffusion mechanism, which was usually used to explain the auto diffusion of Si atoms during the growth of GaAs/Si epilayer. It was reported by Freundlich *et al.* that the preferential diffusion channels for Si incorporation in the GaAs/Si epilayers exist, and the density of these diffusion channels is consistent with the dislocation density.[11] It is evidenced that the PH_3 plasma exposure not only formed a passivating cover layer of gallium phosphide on the surface of GaAs/Si, but also resulted in an enhanced diffusion of P atoms deep into the epilayer due to the high concentration of dislocations in the heteroepitaxial layer. As a result, the electrical activity of dislocation line-related recombination centers was effec-

TABLE I. Photovoltaic properties and DSD of GaAs/Si solar cells under 1 sun AMO illumination at 27 °C before and after PH_3 plasma exposure.

Sample No.	DSD (cm^{-2})	V_{oc} (V)	E_{ff} (%)
As-grown cell	7×10^6	0.85	15.9
PH_3 plasma exposed cell	3×10^6	0.93	18.6

tively passivated by the incorporation of P atoms as isoelectronic dopants. The isoelectronic solution additions in a GaAs crystal are expected to have some effects on the electronic states of dislocations and passivate it.[12]

Usually, dislocations in GaAs/Si solar cells show degradation in both short-circuit current density and open-circuit voltage (V_{oc}), but mostly in the open-circuit voltage.[13] It is believed that the key to improve the efficiency of GaAs/Si solar cells lies in increasing the V_{oc}. The photovoltaic properties of GaAs/Si solar cells[6] and the measured DSD from the EBIC image (as shown in Fig. 1) before and after PH_3 plasma exposure are summarized in Table I. It is clearly seen that, compared with that of the as-grown solar cell ($V_{oc} = 0.85$ V), the PH_3 plasma exposed GaAs/Si solar cell show a very high V_{oc}(0.93 V), and the increase in V_{oc} is consistent with the reduction in DSD. As a result, PH_3 plasma exposure leads to a large improvement in the efficiency, up to 18.6%, due to the large increase in V_{oc}. As proposed by Zolper *et al.*,[14] the decrease in V_{oc} of GaAs solar cells on Si is explained by the formation of low-voltage dislocation line Schottky diodes or heterojunction with the gold metallization or conductive substrate at the *n*-type GaAs surface. The large increase in the V_{oc} of PH_3 plasma passivated GaAs/Si solar cells can be only be explained by the effective passivation of electrical activity of the dislocation-related recombination centers in the active region of GaAs/Si solar cells by the incorporation of P atoms around the dislocation cores, which largely decreased the DSD seen in the EBIC image. Our results indicate that the incorporated P atoms in the GaAs/Si solar cells strongly affected the electronic states of dislocations, and contributed to increase of V_{oc}.

In summary, the phosphidization effects on dislocations in GaAs/Si solar cells by PH_3 plasma exposure were studied. An enhanced diffusion of P atoms in GaAs/Si epilayers during PH_3 plasma exposure was first found, which is thought to be strongly related to the high density of dislocations that existed in the heteroepitaxial GaAs layer. The incorporated P atoms during PH_3 plasma exposure enhanced the passivation effect on dislocation-related recombination centers in the active region of GaAs/Si solar cells, which was directly observed in the EBIC image measurement. As a result, the photovoltaic properties, especially the V_{oc} of GaAs/Si solar cells were effectively improved after the PH_3 plasma exposure.

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