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Hydrogen plasma passivation of GaAs on Si substrates for solar cell fabrication

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The effects of hydrogen plasma treatment and postannealing on GaAs solar cells on Si substrates have been investigated. It is found that postannealing temperature is an important parameter to obtain GaAs on Si with a long minority carrier lifetime. The minority carrier lifetime is increased and the deep level concentration is decreased by the hydrogen plasma treatment. Even after 450 °C postannealing with the complete recovery of the shallow impurity level, the minority carrier lifetime is still longer and the deep level concentration is lower than those of the as-grown sample. It means that the defects in GaAs on Si are passivated by hydrogen. The efficiency of GaAs-on-Si solar cell (air mass 0, 1 sun) is improved from 16.6% (as-grown) to 18.3% by the hydrogen plasma passivation and to 17.2% by the hydrogen plasma passivation and postannealing at 450 °C.

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I. INTRODUCTION

The crystal growth of GaAs on Si substrates has been studied for more than two decades and several classes of devices such as solar cells,\textsuperscript{1} lasers,\textsuperscript{2} and field effect transistors\textsuperscript{3} have been fabricated. Much effort has been devoted to reduce the dislocation density by using strained layer superlattices,\textsuperscript{4} thermal cycle annealing (TCA),\textsuperscript{5} selective epitaxy,\textsuperscript{6} and so on. However, the problem of high dislocation densities which are generated due to lattice mismatch and thermal expansion mismatch has not been solved yet. For example, although the dislocation density should be reduced to as low as $10^5 \text{cm}^{-2}$ in order to obtain high efficiency GaAs solar cells on Si substrates,\textsuperscript{7} reproducibly reported dislocation densities are on the order of $10^6 \text{cm}^{-2}$.

Another way to improve the crystal quality of GaAs on Si is to electrically passivate the dislocations. Although considerable efforts have been made to reduce the dislocation densities, methods involving the passivation of the dislocations attracted much less attention. The most familiar technique is hydrogen passivation, which is usually applied in polycrystalline silicon technology. Improved Schottky diode characteristics, thermal stability, and photoluminescence properties of GaAs layers grown on Si have been reported by using hydrogen passivation.\textsuperscript{8–10} However, there has been no report on the effect of hydrogen passivation for GaAs \textit{pn} junctions or for GaAs solar cells grown on Si substrates.

In a previous article, we reported that the minority carrier lifetime of GaAs on Si is improved by hydrogenation.\textsuperscript{11} In this article, we describe the improvement of minority carrier properties and GaAs \textit{pn} junction solar cell efficiencies by hydrogenation coupled with various postannealing temperatures.

II. EXPERIMENT

GaAs layers were grown on (001) Si substrates misoriented 2° off towards [110] by conventional atmospheric pressure metalorganic chemical vapor deposition (MOCVD) using a two-step growth method which utilizes a low temperature (400°C) grown, 10-nm-thick buffer layer. Trimethylgallium, trimethylaluminum, diethylzinc, arsine (AsH$_3$), and hydrogen selenide were used as the source materials for Ga, Al, Zn, As, and Se, respectively. Hydrogenation was carried out in a quartz tube, where a hydrogen plasma was excited by rf power via a copper coil encircling the quartz tube. The plasma power, the treatment time and the substrate temperature during the plasma treatment were 90 W, 2 h, and 250 °C, respectively. In order to recover shallow level passivation and the damage induced by the plasma treatment, postannealing was performed in an AsH$_3$+H$_2$ ambient at various temperatures ranging from 350 to 750 °C for 10 min. Electrochemical capacitance–voltage measurement, photoluminescence (PL) at 4.2 K using an Ar ion laser, and deep level transient spectroscopy (DLTS) were performed on 3-\textmu m-thick films. Gold Schottky contacts were made for DLTS measurements. Al$_{0.8}$Ga$_{0.2}$As (50 nm)/GaAs (1 \textmu m)/Al$_{0.8}$Ga$_{0.2}$As (50 nm) double heterostructures were fabricated to determine the minority carrier lifetime by time resolved PL. The structure of the solar cell is schematically shown in Fig. 1. It is a simple heterostructure solar cell with a total area and an active area of 25 and 22.05 mm$^2$, respectively. The growth sequence and the device fabrication are the same as reported previously except for the TCA temperature and Al composition.\textsuperscript{12,13} The growth temperature and the
maxima of TCA temperature were kept constant to 750 and 900 °C, respectively. After growing a 0.7-μm-thick GaAs layer on a Si substrate, TCA (two times), a 0.7-μm-thick GaAs growth, TCA (three times), and a 0.1-μm-thick GaAs growth were performed sequentially. The surface of the cell was coated with a ZnS/MgF2 antireflection coating. Furnace annealing was performed at 380 °C for 30 s to make a low resistivity ohmic contact in nitrogen ambient. The photovoltaic properties were measured under air mass AM0, 1 sun conditions at 27 °C. The efficiency was calculated on the basis of active area.

III. RESULTS AND DISCUSSION

A. Effect of hydrogenation and postannealing

Carrier concentration profiles of unintentionally doped GaAs grown on Si substrates, before and after hydrogenation, are shown in Fig. 2. Undoped GaAs-on-Si is n type \((1 \times 10^{17} \text{ cm}^{-3})\) due to Si autodoping during the growth.\(^{14}\) For the hydrogenated sample, the carrier concentration is reduced to about \(3 \times 10^{16} \text{ cm}^{-3}\) at depth exceeding 1 μm. This is due to the electrical passivation of the shallow levels. Since the major donor in GaAs grown on Si substrates is Si via autodoping from the substrate, passivation will occur by the formation of SiH\(_0\) samples via the reaction

\[
\text{Si}^+ + \text{H}^0 + e^- \rightarrow \text{SiH}^0.
\]

The SiH\(_0\) complex will then be dissociated by heat or applied electric fields. There is a kink in the concentration profile curve at a depth of nearly 0.8 μm which corresponds to the plasma-induced damage,\(^{15}\) since the knee goes deeper with increased plasma treatment time. After a 10 min annealing at 450 °C in AsH\(_3\)+H\(_2\) ambient, the donor electrical activities were completely restored to their initial levels. Comparable 400 °C annealing is not sufficient.\(^{11}\)

Figure 3 shows the 4.2 K PL spectra of GaAs on Si for as-grown sample, hydrogenated sample, hydrogenated sample annealed at 450 °C, and hydrogenated sample annealed at 700 °C. The major peaks are peak B corresponding to the heavy hole-associated free excitation and peak C corresponding to the carbon impurity-bound exciton. After the sample is treated by the hydrogen plasma, the full width at half maximum (FWHM) of peak B narrows from 4.49 to
3.83 meV. This narrowing is due to the passivation of localized states. With 450 °C annealing where the shallow level is completely recovered, the FWHM is a little narrower than that of the as-grown sample. Moreover, even with 700 °C annealing, the FWHM is narrower than that of the as-grown sample, however, the additional peak D, which corresponds to the impurity or defects, and E appear. The origin of peaks D and E is not clear at present, but it appears due to defects created during the plasma passivation. These peaks do not appear during the annealing under an AsH$_3$+H$_2$ atmosphere.

Figure 4 shows the minority carrier lifetime derived from the time resolved PL decay curve. The minority carrier lifetime increases from 1.66 (as-grown) to 4.66 ns after the plasma treatment, and gradually decreases with increasing annealing temperature. It is difficult to judge the crystal quality only by the minority carrier lifetime because the lifetime is also affected by the shallow carrier concentration. In Fig. 2, the shallow carrier concentration of the 450 °C annealed sample is the same as that of the as-grown sample, since with passivation the shallow level is completely restored. The minority carrier lifetime after hydrogen plasma treatment followed by annealing at 450 °C (2.27 ns) is longer than that of the as grown sample (1.66 ns), suggesting that the defects generated by lattice mismatch and thermal expansion mismatch are electrically and optically passivated. The longer minority carrier lifetime of the hydrogenated sample (before annealing) is due to defect passivation and shallow level passivation. This is the first observation of hydrogen passivation of the heteroepitaxial defects, evidenced by the minority carrier lifetime improvement for MOCVD grown GaAs-on-Si. The decreased minority carrier lifetime at higher annealing temperatures has been examined. Species in the plasma include free radicals, ions, and electrons. Among these species, free radicals can effectively passivate the defects. Furthermore, it is well known that ions can damage the semiconductor surface. Therefore, during the hydrogenation process, defect passivation, and damage formation are taking place at the same time. The minority carrier lifetime of the hydrogenated sample annealed at 450 °C is longer than that of the as-grown sample, since the defects generated during the plasma treatment are passivated. On the other hand, after 650 °C annealing, the hydrogen which passivated the defects is desorbed, resulting in minority carrier lifetime degradation.

The effects of deep level passivation were characterized by DLTS using Schottky diodes. The DLTS spectra of an as-grown sample, a hydrogenated sample, and a hydrogenated sample annealed at 450 °C are shown in Fig. 5. One relatively sharp peak at about 380 K and one broad peak at about 280 K are observed. The former is EL2 which is usually observed in MOCVD-grown GaAs. The latter is due to a deep level related to a Si-defect complex. It is clearly observed that the DLTS peak of the Si-defect related level becomes smaller after hydrogen plasma treatment. It suggests that the Si-related defect level is passivated by hydrogenation. The passivation effect remains even after 450 °C annealing where the shallow level is completely restored.

From the earlier experiments we can conclude that (1) the shallow level which has been passivated by hydrogenation is completely recovered by annealing at 450 °C in AsH$_3$+H$_2$ ambient, (2) the deep levels are still passivated by hydrogen after annealing at 450 °C in AsH$_3$+H$_2$ ambient, and (3) hydrogenation followed by 450 °C annealing produces a longer minority carrier lifetime at the same shallow carrier concentration.

B. Hydrogenation of GaAs solar cells grown on Si substrates

Table I shows the photovoltaic properties (short circuit current density $J_{sc}$, open circuit voltage $V_{oc}$, fill factor FF and conversion efficiency $\eta$) of a GaAs solar cell on a Si substrate for various hydrogen plasma treatment and anneal-
Further improvement is expected following optimization of the hydrogen plasma conditions.

IV. CONCLUSION

The effects of hydrogenation and postannealing for GaAs grown on Si substrates were investigated. When the sample was treated with a hydrogen plasma, shallow levels and deep levels were passivated, resulting in an increased minority carrier lifetime. Shallow level passivation was recovered by postannealing at 450 °C in AsH₃+H₂ ambient while deep level passivation was retained. The conversion efficiency of GaAs-on-Si was found to be increased from 16.6% (as-grown) to 17.2% by hydrogen plasma treatment and 450 °C postannealing, and to 18.3% by hydrogenation alone. Hydrogen passivation is therefore a potential method to obtain high efficiency GaAs solar cells on Si substrates.

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