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Surface passivation of nitride- and phosphide-based compound semiconductors

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Results of surface passivation treatments on nitride and phosphide compound semiconductors are described. In order to assess why sulphur-based passivation treatments are not equally effective on all semiconductors we carried out sulphur passivation using both liquid phase and gas phase techniques and found that the former is more effective than the latter. An explanation in terms of surface ionicity is provided. The improvement as seen through the DC current gain of heterojunction bipolar transistors is described as is its temporal behaviour. Experiments with nitride semiconductors show that silicon nitride is more effective as a surface passivation than any type of sulphide treatment, for this family of semiconductors. The temporal behaviour of silicon nitride passivation on gallium nitride is described. Finally, the use of silicon nitride conformal films for topography-intensive devices has been demonstrated.

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1. Introduction

Compound semiconductor devices based on the III-nitride and III-phosphide families are now widely used and investigated. This is because of the outstanding properties of these semiconductors for fabricating specific classes of devices. The wide band gap of gallium nitride, for instance, makes possible the realization of short wavelength light emitters such as blue and UV LEDs as well as lasers, in addition to solar blind photo detectors and high power RF transistors. The small band gap coupled with exceptional carrier transport properties of indium phosphide and related alloys, on the other hand, make it possible to fabricate high performance, high frequency transistors and long wavelength light emitters. Unlike transistors integrated on monolithic chips where devices feature buried junction configurations, compound semiconductor devices have much larger exposed areas. This leaves them vulnerable to surface conduction effects where leakage currents flow through dangling bonds and cause degradation in device performance. Deterioration in device properties include reduction in bipolar transistor breakdown voltage and current gain, increase in junction reverse bias leakage current, increase in the dark current of photo diodes, reduction in the quantum efficiency of LEDs and increase in the threshold current of semiconductor lasers. In order to avoid such undesirable effects the broken bond pathways on semiconductor surfaces must be effectively blocked. The usual way to do this is to passivate surfaces with a suitable chemical species that can form bonds with surface dangling bonds and thus remove them as a channel for extraneous electrical conduction. Here we report on our work that was undertaken to determine effective and lasting passivation treatments for III-nitrides and III-phosphides. Our work has also thrown light on the mechanisms involved in surface passivation and will, therefore, be useful for assessing the effectiveness of different surface treatment techniques.

2. Passivation of III-Phosphides

Indium phosphide-based heterojunction materials are used for the fabrication of Heterojunction Bipolar Transistors (HBTs) [1,2], semiconductor lasers, infrared LEDs and p-i-n photo diodes. Obviously, this material and its extended ternary and quarternary alloys are extremely important from an application point of view. Several methods have been developed to passivate InP devices. Caffin et al. [3] have reported a double heterojunction InP/InGaAs HBT fabrication process with polyimide passivation and planarization that enables fabrication of high bit-rate circuits, such as 36 Gb/s 2:1 multiplexers. Other workers have compared the use of silicon dioxide and silicon nitride for passivating InP HBTs and found that with the former the Fermi level is pinned near the conduction band edge of InP whereas the latter results in pinning at the mid-gap position and thus improving the device leakage characteristics [4]. The degradation of InP/InGaAs/InP double heterojunction bipolar transistors was studied by Hong Wang and colleagues [5] and they found that silicon nitride passivation is more effective in improving some device characteristics but less effective for others. Another work has described the use of Bisbenocyclobutene (BCB) in preference to silicon nitride and presented measurements of improved high frequency operating characteristics [6]. Native oxide films grown by Liquid Phase Epitaxy (LPE) have been described as a means of passivating p+-GaAs, n-InGaAs and n-InGaP epitaxial films by Sze and colleagues. They found significant improvements in current gain and leakage current of InGaP/GaAs HBTs [7].

In our work we made use of InP/InGaAs single heterojunction bipolar transistor epitaxial stacks grown through MOCVD as the base material to investigate passivation treatments on III-phosphides. We made use of silicon nitride elsewhere in the HBT fabrication process but not for device passivation which was entirely carried out by sulphide treatments. Sulphur-based passivation treatments have been earlier reported to cause effective passivation of InP devices, especially HBTs [8-10]. A simplified scheme of our epitaxial structure is shown in Fig. 1.

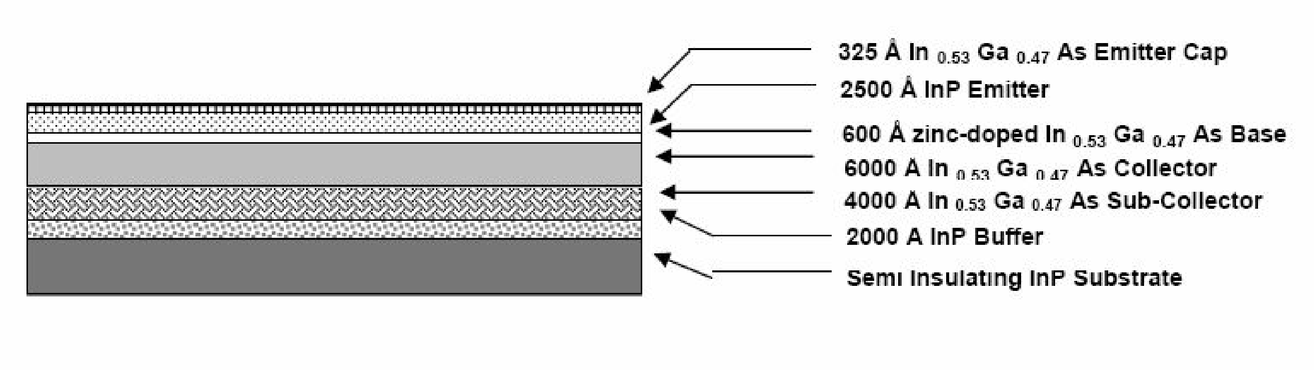

Fig. 1. Simplified epitaxial layer structure of the InP/InGaAs HBT stack used in this work.

Our experiments were designed to expose InP/InGaAs stack with sulphur species from both gaseous and liquid ambients. The former was done using a stream of hydrogen sulphide (H_2S) gas whereas the latter was accomplished with a solution of inorganic sulphides in water. A comparison between these two application methods has not been reported in the literature before. In the first case the passivating species were individual H_2S molecules while in the second case these were solvated sulphide ions. Both passivated devices and control devices without any passivation treatments were measured to assess the effectiveness of different passivation treatments.

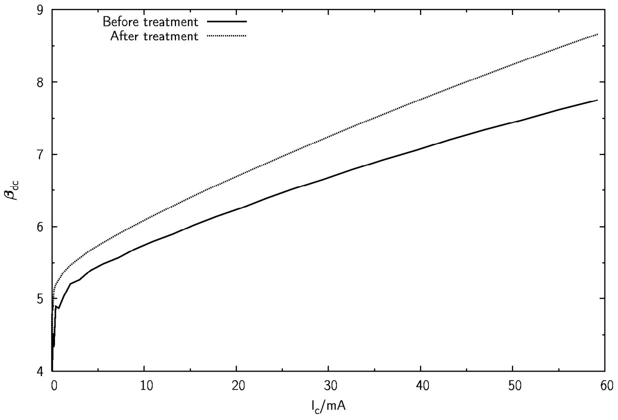

Fig. 2. Plot of HBT reverse biased emitter-base junction leakage current as a function of time for a liquid-phase sulphide passivated device.

Hydrogen sulphide gas was generated by reacting sodium sulphide with dilute hydrochloric acid. An HBT die was cleaned using the usual wet clean process (rinsing in high purity water, isopropyl alcohol, methanol and acetone) and was then dipped in dilute HCl to remove the thin film of native oxide that forms on the surface of the semiconductor. The HBT chip was then exposed to the stream of H_2S for different lengths of time. Further details of this process have been described elsewhere [11]. Liquid phase passivation was carried out simply by immersing an HBT die in a 30% solution of ammonium sulphide in water. We found that the liquid phase process was much more effective than the gas phase process and in the measurement described below only liquid phase treated devices were used.

Transistor junction leakage current and HBT DC common-emitter current gain were measured as the principal assessment parameters and measurements were taken as a function of time. The change in current gain of an HBT after an aqueous ammonium sulphide treatment is shown in Fig. 2 here. It can be seen that the current gain shows a marked improvement that increases with increase in I_c. The improvement in β_{dc} is directly proportional to the collector current flowing through the device. The improvement in current gain from the passivation process is not permanent unless the surface is sealed with a suitable encapsulation material. We measured the changes in β_{dc} for a passivated device over a period of several weeks and found the results depicted here in figure 3. The improved DC current gain is seen to decrease by about 3.5% over a period of 45 days.

3. Passivation of III-Nitrides

Gallium nitride-based heterojunction materials have become extremely important for optoelectronic applications. GaN, together with higher alloys such as InGaN and AlGaN are now widely used for making short wavelength LEDs and lasers. Other applications, such as bipolar and field effect transistors, are relatively limited but are also growing gradually. Similar to phosphide semiconductor devices, nitride-based devices too suffer from detrimental effects from skin leakage. In agreement with prior work by others, we have found that sulphur-based treatments are not as effective with nitrides as they are with phosphides. The reason for this is clear from the work described above where liquid phase passivation was found to be much more effective than gas phase passivation. This has to do with the low charge separation in the Ga-N bond system which causes smaller residual multipole electric fields and thus rather weakly attracts passivating species. The preferred way to passivate nitride surfaces is to put down a layer of either silicon dioxide or silicon nitride through a PECVD process. Silicon nitride passivation is also used for silicon integrated circuits. In this case, bond defects in either SiO_2 or Si_3N_4 that result from broken bonds at the interface between these materials and GaN combine with GaN dangling bonds and cause surface passivation. Again, these materials work effectively for passivating silicon-based integrated circuits because of the same reasons.

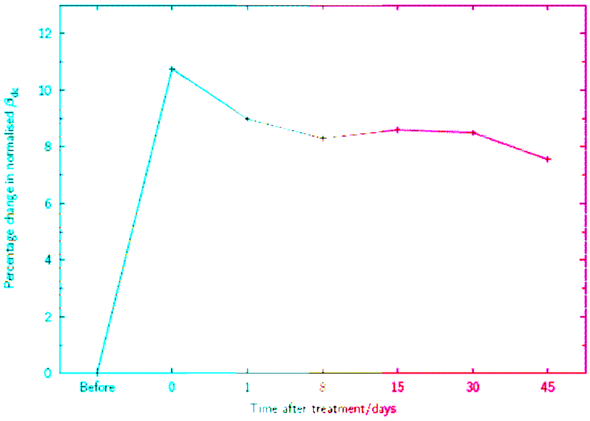

Fig. 3. Plot of HBT DC current gain (β) as a function of time for a liquid-phase sulphide passivated device.

For the sake of comparison, we investigated sulphide treatments with ammonium sulphide and sodium sulphide solutions as well because chalcogenide passivation is successfully used with both GaAs and InP-based devices. Our experiments on surface resistance were carried out on GaN epilayer samples carrying a two-dimensional pattern of Ti/Au non-alloyed surface contacts. This is shown in figure 4 here. Non-alloyed contacts are best for this type of measurement because they have no material mixing with the semiconductor so that the contacts only probe the surface of the semiconductor. For contacts spaced 375 μm apart on GaN epilayer we measured surface resistances in the range of 4 MΩ to 4.5 MΩ. After surface passivation with sodium sulphide solution surface resistances in the range of 6 MΩ to 7 MΩ were observed whereas after surface passivation with ammonium sulphide solution (this is commercially available from Sigma-Aldrich as a 20 weight percent aqueous solution of ammonium sulphide gas in water) the surface resistances were found to be in the range of 7 MΩ to 7.5 MΩ. These resistance values for passivated surfaces decreased over time. As with InP and other semiconductors the temporal decrease is attributed to the loss of sulphur as the sulphur atoms are only weakly bonded to semiconductor surface atoms. We next tested silicon nitride passivation. Our results indicate that silicon nitride deposition works best in that the passivation effects are both large (as measured through contact-to-contact leakage resistances) and long lasting. Surface contact-to-contact resistance with silicon nitride passivation film between contacts, can reach several tens to hundreds of MΩ. Silicon nitride passivation has been previously reported to improve current collapse in GaN/AlGaN high electron mobility transistors [12] and to improve noise and breakdown performance in GaN heterostructure transistors [13]. We used Plasma Enhanced Chemical Vapour Deposition (PECVD) in an Inductively Coupled Plasma (ICP) reactor to deposit high quality silicon nitride layers on GaN surfaces. The ICP-PECVD process is superior to other CVD processes because it is fast (due to the high ion density in the resulting plasma) and operates at a low temperature. Contact patterns were lithographically produced and access windows etched to expose GaN surface at contact pad locations. Contact metallization and lift-off were performed followed by contact annealing. Resistance measurements performed using semiconductor parameter analysers have shown resistances two to three orders of magnitude higher than with other passivation techniques mentioned earlier. Another benefit of silicon nitride passivation is its permanency. Fig. 5 shows the changes in inter-contact resistance for our silicon nitride coated GaN sample as a function of time. Further work is being carried out to understand the passivation mechanism and to develop reproducible passivation techniques with silicon nitride.

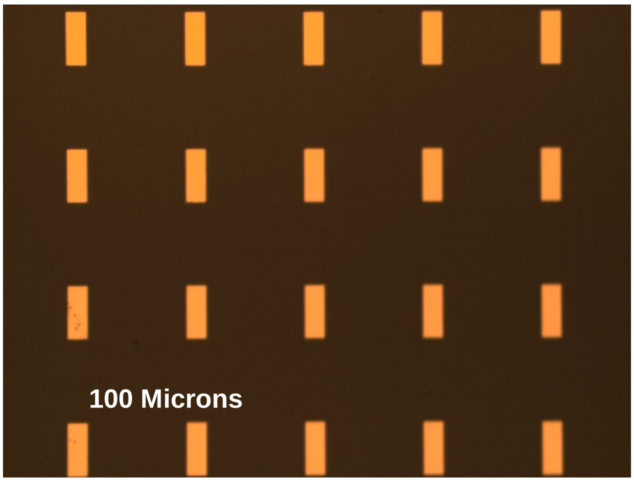

Fig. 4. Contact pad structure on a 25 μ thick epilayer of GaN used for surface resistance measurements at room temperature. The metal pads are un-annealed Ti/Au bi- layers separated by 375 μ gaps.

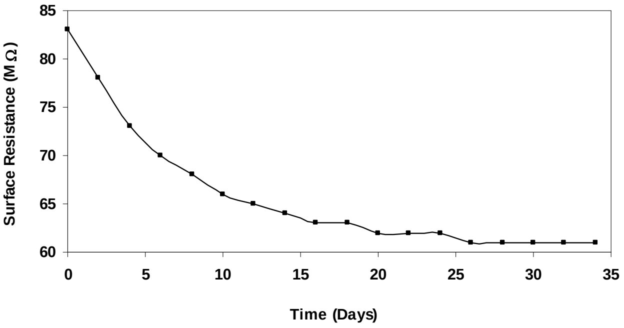

Fig. 5. Plot of surface resistance variation over time for silicon nitride passivated gallium nitride.

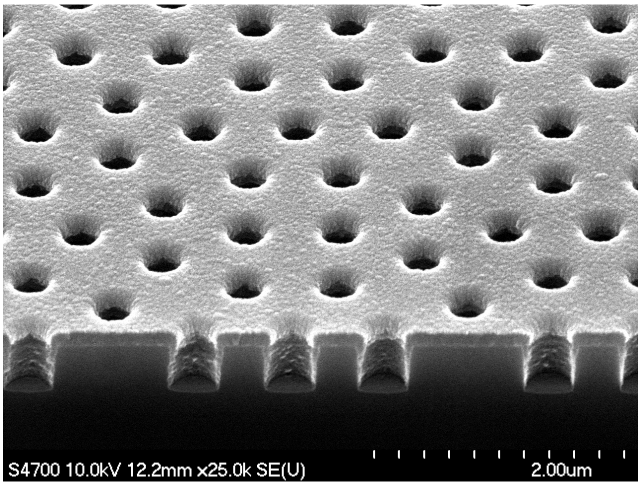

Fig. 6. Cross-sectional SEM micrograph showing surface and hole side wall coverage with conformal PECVD silicon nitride film.

Our PECVD silicon nitride deposition process showed very good gap and trench filling characteristics. As high aspect ratio topographic features are increasingly becoming common place in semiconductor device technology so the use of low temperature CVD Si_3N_4 films could be advantageously integrated with process flows. An example is shown here in figure 6 where a PECVD silicon nitride film is seen covering both the top surface and the etched hole side walls of a photonic crystal structure in GaN LED material. Without hole wall passivation LEDs with etched light extraction structures can exhibit reduced quantum efficiency due to non-radiative surface recombinations on wall surfaces but coating the walls with a thin transparent layer of silicon nitride avoids such non-radiative energy loss. Our silicon nitride films have low intrinsic stress so they show neither cracking (caused by excessive tensile stress) nor buckling or delamination (caused by excessive compressive stress).

4. Conclusions

The results of our work show that there is no single passivation treatment which works best with all semiconductors. The surface dipolar behaviour determines the choice of the passivating material. High ionicity surfaces such as arsenides, antimonides and phosphides passivate well with sulphur-based passivation techniques. Nitride semiconductors (as well as silicon and silicon-germanium alloys) are not well-passivated by sulphide passivation treatments but fare well with silicon nitride passivation films deposited by PECVD processes. Furthermore, silicon nitride can be conformally deposited over undulating topography and sub-micron holes enhancing its utility for manufacturing LEDs with photonic crystal structures for light extraction or beam shaping.

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