Passivation of GaAs/AlGaAs heterojunction bipolar transistors by S_2Cl_2 solution

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(Received 17 July 1996; accepted for publication 3 December 1996)

The diluted S_2Cl_2 solution has been employed to treat the GaAs/AlGaAs heterojunction bipolar transistors. It is shown that the dc characteristics of the transistor could be improved significantly and the passivation effect is not subject to degradation by heating to 150 °C in atmospheric air and immersing in water. A real-time monitoring technique is proposed which provides good control of the passivation stopping point. © *1997 American Institute of Physics.*
[S0003-6951(97)02306-1]

Surface passivation of III-V compound semiconductors especially GaAs is an important and unsolved problem in the device technology. Since Sandroff *et al.*[1] proposed the sulfur passivation of GaAs by using $Na_2S\cdot 9H_2O$ solution dipping, a variety of S-passivation techniques have been reported. Among them, there are liquid phase treatments [such as dipping in $(NH_4)_2S_x$ solution,[2–4] $(NH_4)_2S+P_2O_5$,[5] electrochemical S-passivation],[6] gas phase treatments (such as H_2S treatment,[7] ultraviolet photosulfidation),[8] and epitaxial growth of gallium sulfide by metal organic chemical vapor deposition.[9] But none of these techniques has been applied to passivate the practical GaAs devices except the earlier work by Sandroff *et al.*,[1] where an enhancement of the current gain of a GaAs/AlGaAs heterojunction bipolar transistor (HBT) by a factor of 60 after the S treatment was demonstrated. However, it was found later that the passivation effect by dipping in $Na_2S\cdot 9H_2O$ or $(NH_4)_2S_x$ solution is unstable, which prohibits the practical use of these methods in the devices technology. The main cause of the degradation is the reoxidation of the S-passivated surface under the exposure in atmospheric ambient.

In our previous work, a new sulfur passivation technique was developed by using an oxygen-free S_2Cl_2 solution to replace the ordinary $(NH_4)_2S_x$ solution.[10] The advantages of S_2Cl_2 passivation are the effectiveness of removing the native oxide of GaAs and the prevent of oxygen uptake on the S_2Cl_2 treated GaAs surface even after exposed in atmospheric air for several days or immersing in de-ionized water for 40 h. This technique has been employed as an effective substrate treatment in the epitaxial growth of ZnSe on GaAs, where improvement of the crystalline quality of the epilayer and the perfection of heterointerface was illustrated.[11] In this work, the S_2Cl_2 passivation technique is applied to treat the AlGaAs/GaAs HBT. The improvement of the overall dc characteristics of the HBTs is demonstrated. A real-time monitoring of the treating process is proposed to optimize the passivation condition.

The HBT samples were provided by a production pilot line. The transistor chip was mounted on a holder without package. The cross section of the device structure is schematically shown in Fig. 1. The n-p^+-n type HBT was grown by the molecular beam epitaxy on a semi-insulating GaAs substrate. The collector, base, and emitter regions are n^+/n-GaAs, p^+-GaAs, and n-AlGaAs, respectively. The doping concentrations in the n-GaAs, p^+-GaAs, and n-AlGaAs are 4×10^{16} cm^{-3}, 2×10^{19} cm^{-3}, and 5×10^{17} cm^{-3}, respectively. The thickness of the p^+-GaAs base region is 100 nm. The transistor is basically a mesa structure device with the active areas surrounded by the proton implanted GaAs insulating layer (shown as hatched areas in Fig. 1). The dark areas are the metal electrodes. To avoid the short circuit between emitter and base, a part of the periphery of the e-b junction with a width of 2 μm and length of 5 μm is exposed to atmosphere. Although a protection layer such as the polyimide can be deposited on the exposed e-b junction periphery to avoid the further degradation of the e-b characteristics, the non-passivated e-b junction is inevitably affected by the relatively large amount of recombination centers which exist on the surface of the e-b junction. Thus, by using the S passivation, it is the purpose of this work to greatly suppress the surface recombination velocity and hopefully to improve the characteristics of the HBT.

The passivation process was carried out by simply dipping the HBT wafer in a solution of $S_2Cl_2:CCl_4=1:4$ at room temperature for 15–30 s after it was ultrasonically cleaned by acetone, ethanol, and de-ionized water sequentially and dried by flowing N_2. The passivation was stopped by rinsing in CCl_4, acetone, ethanol, and de-ionized water, and N_2 blowing sequentially. The passivation effects on several typical HBT samples are listed in Table I, where the enhancement of the dc current gain h_{FE} by a factor of 3–8,

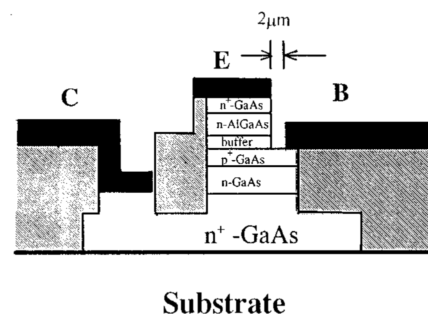

FIG. 1. Schematic cross section of the GaAs/AlGaAs HBT device.

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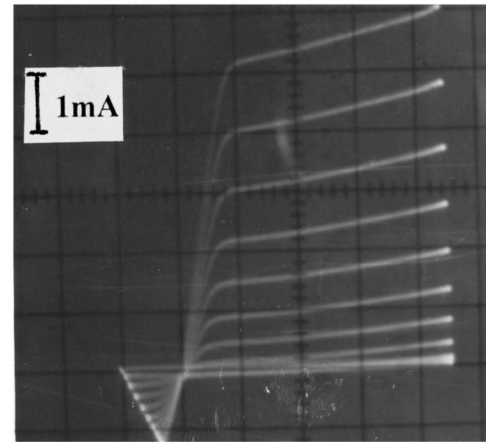
TABLE I. The improvement of the dc characteristics of HBTs after S_2Cl_2 solution treatment. (h_{FE}) common-emitter dc current gain, (I_b^m) minimum base injection current, (V_{off}) offset voltage, (R_s) series resistance, (B.F.) before passivation, (A.F.) after passivation.

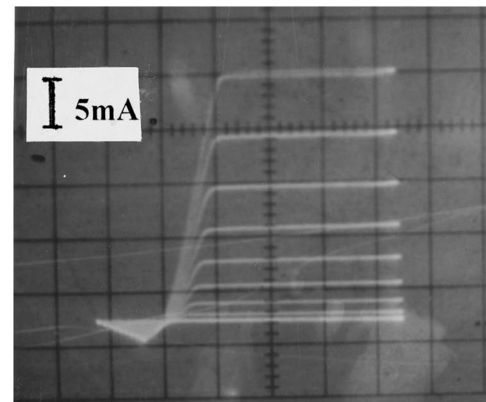
	I_b	h_{FE}		I_b^m (μA)		V_{off}(V)		R_s (Ω)	
Sample	(μA)	B.P.	A.P.	B.P.	A.P.	B.P.	A.P.	B.P.	A.P.
1	70	20	90	20	10	0.6	0.5	200	120
2	70	18	90	40	30	1.0	0.7	250	110
3	250	80	400	150	60	1.0	0.3	26	11
4	100	25	80	60	40	0.5	0.2	23	11
5	100	1.3	10	100	10	0.7	0.4	330	240

and a decrease of the minimum base injection current by a factor of 1.3–10 are demonstrated. In addition the offset voltage V_{off} and the series resistance R_s in the saturation region of the output characteristic are also decreased. It means that the overall dc characteristics of the HBTs are improved remarkably. Although the enhancement of h_{FE} is not as large as 60 as reported by Sandroff *et al.*, it is related to the intrinsic design of the HBT. Therefore, it does not mean that the passivation of S_2Cl_2 used here is not as good as that of $Na_2S \cdot 9H_2O$ as reported by Sandroff *et al.* The transistors we studied are the real devices used in the microwave applications. In order to obtain good reproducibility and high yield in manufacturing, the base region of the HBT was controlled not to be very thin with a designed h_{FE} not larger than 500. Actually the samples used here are those unqualified transistors. As seen in Table I, the largest h_{FE} obtained after S_2Cl_2 treatment is 400, which is very close to the designed value.

Since the S-containing solution S_2Cl_2 or $(NH_4)_2S_x$ can etch away GaAs in addition to the passivation of its surface, the S treatment should be carefully controlled to achieve sufficient passivation, but not to remove too much of the GaAs layer. Under-treatment or over-treatment both lead to unsatisfactory results. Actually, the proper etching time is different for different types of HBTs. We develop a real-time passivation control by measuring the dc characteristics during immersion of the transistor in a solution of $S_2Cl_2:CCl_4 = 1:100$. A video camera records the variation of the output characteristics of the HBT as a function of time. Figure 2 shows the common-emitter characteristics of a transistor before passivation treatment at room temperature (a), and liquid nitrogen temperature (b). The dc current gain at the base injection current of 100 μA increases from the room temperature value of 20 to 100 at LN_2 temperature. This results from the reduction of the surface recombination velocity at low temperature. This also indicates that the surface of the *e-b* junction is not well passivated. Therefore, the S treatment gives a pronounced effect on the current gain of this HBT as shown by Fig. 2(c), where the room temperature dc current gain increases to 90. The real-time monitoring shows a relationship between the current gain and the passivation time as shown in Fig. 3. The initial slow increase of h_{FE} corresponds to the removal of the native oxide on the GaAs surface by S_2Cl_2. The steep rise of h_{FE} corresponds to the formation of sulfides. h_{FE} decreases slowly after it reaches a maximum, which is a result from the over etching of GaAs. From above results, it is possible to control the passivation time. The S_2Cl_2 passivation condition can be optimized by stopping the dipping as long as the current gain does not increase further. This real-time monitoring cannot be realized by using an ordinary $Na_2S \cdot 9H_2O$ or $(NH_4)_2S_x$ solution because the ionic conductance of the aqueous solution make



(a)



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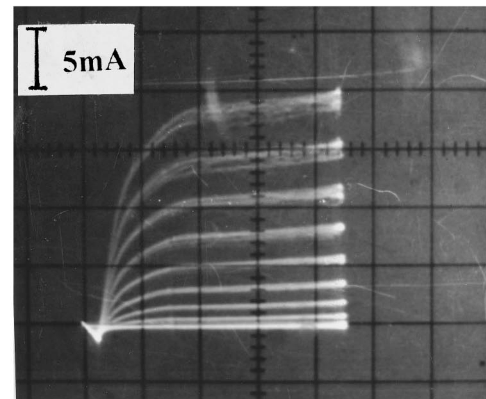

(c)

FIG. 2. Common emitter characteristics for (a) an unpassivated HBT at RT ($I_b = 20$ μA/div, $I_c = 1$ mA/div, $V_{bc} = 0.5$ V/div). (b) The transistor at LN_2 temperature ($I_b = 20$ μA/div, $I_c = 5$ mA/div, $V_{bc} = 0.5$ V/div). (c) The same transistor after S_2Cl_2 passivation at RT ($I_b = 20$ μA/div, $I_c = 5$ mA/div, $V_{bc} = 0.5$ V/div).

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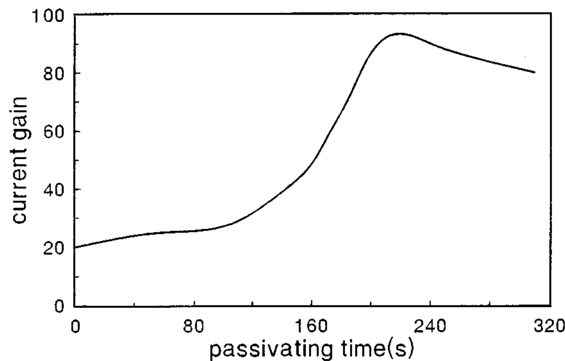

FIG. 3. Current gain of HBT vs S_2Cl_2 passivating time.

the *in situ* measurement of the dc characteristics of HBT impossible. This problem does not happen in the case of the $S_2Cl_2 + CCl_4$ solution due to its very poor ionic conductance.

The stability of the S_2Cl_2 treatment is tested by heating the passivated HBT to 150 °C in air for 20 min followed by immersing in de-ionized water for 24 h. Both heating and immersing are used to strengthen the uptake of oxygen on the surface. But no degradation of the dc characteristics of the device is observed. However, the S_2Cl_2 passivation alone cannot solve the problem of longevity by long time exposure in air ambient since the S-containing layer formed by S_2Cl_2 dipping is too thin.[10] It is expected that by coating a protection film further on the S_2Cl_2 passivated surface, the longevity of this passivation would be achieved.

We did the photoemission measurements on the S_2Cl_2 treated GaAs wafers to investigate whether the passivation effect is related to the removal of the Fermi level pinning. The results (not shown here) indicate that the Fermi level still pins near the midgap after the S_2Cl_2 treatment, which agrees well with previous work.[12,13] It implies that the passivation effect is basically related to the reduction of surface recombination velocity by the S_2Cl_2 treatment.

In conclusion, the diluted $S_2Cl_2 + CCl_4$ solution is used to treat the exposed *e-b* junction of a GaAs/AlGaAs heterojunction bipolar transistor. Significant improvement of its dc characteristics has been achieved. The S_2Cl_2 passivation could be benefited further by using a real-time monitoring method to optimize the passivation condition.

This work was partially supported by the National Natural Science Foundation of China.

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