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We have investigated the dark current-voltage characteristics of GaAs *pn* homojunctions whose surfaces have been passivated with Na₂S and (NH₄)₂S chemical treatments. Reductions in $2kT$ perimeter recombination currents by a factor of 3.2 were obtained for the two treatments. A shunt leakage, observed at low forward bias for the Na₂S treated devices, is virtually eliminated with the (NH₄)₂S treatment. It is also shown that even the high quality, large area (0.25 cm²) *pn* diodes used in this study are dominated by $2kT$ edge currents before passivation.

Due to a large density of surface states the performance of GaAs devices, such as solar cells and heterojunction bipolar transistors (HBT's), can be dominated by recombination at exposed mesa edges. This recombination at the exposed perimeter gives rise to an additional component of forward biased current for a GaAs *pn* diode. The total current in a forward-biased GaAs *pn* junction can be represented as

$$I = J_{01}A\left[e^{qv/kT} - 1\right] + (J_{02B}A + J_{02P}P)\left[e^{qv/2kT} - 1\right].$$
$$(1)$$

The saturation current densities J_{01} and J_{02B} are associated with carrier recombination in the quasi-neutral and bulk space-charge regions, respectively, and A is the area of the *pn* junction. The current density J_{02P} is associated with recombination at the exposed mesa edge and P is the perimeter of the *pn* junction. Even for the large square ($A = 0.25$cm²) GaAs diodes reported in this letter, the total perimeter recombination current is much larger than the bulk space-charge recombination current.[1]

The elimination or lowering of surface recombination can therefore significantly reduce the $2kT$ current of a GaAs diode. This reduction in $2kT$ current would result in an increase in gain at a given collector current for a HBT. Lowering of the dark current due to reduction in $2kT$ current of a solar cell will increase the one-sun fill factor and hence increase the efficiency of the cell.[1] The lowering of the $2kT$ perimeter recombination current in *pn* GaAs diodes also allows one to observe the $2kT$ bulk recombination current; thereby studies could be performed to correlate bulk $2kT$ recombination current with defects and impurities, and the possibility of further reduction in $2kT$ current. A reduction in perimeter surface states may also reduce edge generation and increase the storage time of dynamic GaAs memories.[2,3]

Recently, photochemical[4] and chemical[5-8] treatments have been shown to be effective in lowering the surface state density of III-V semiconductors. This reduction of the surface state density unpins the Fermi level at the surface and also reduces the nonradiative recombination at the surface.[6] However, these treatments are far from ideal. They last for only a short time in room air (anywhere from 20 min for the photochemical treatment to 18-48 h for a Na₂S chemical treatment). Another problem with the Na₂S chemical treat-

ment is the introduction of a surface conduction. For a GaAs solar cell or emitter base junction of a HBT, the surface conduction is manifested as a shunt leakage at low forward bias.

While the nature of the semiconductor surface after treatment is not known, it appears that the common link between various chemical treatments is sulfur-containing compounds. The most widely reported compound is Na₂S. It is not known if the other elements of the various sulfide compounds contribute to the nature of the interface or just provide a vehicle to present sulfur to the surface of the semiconductor. Nottenburg *et al.*[8] have investigated the effects of the Na₂S treatment on the dark current-voltage (I-V) characteristics of AlGaAs/GaAs *pn* heterojunctions. In this letter we report the effects of Na₂S and (NH₄)₂S treatments on the dark I-V characteristics of GaAs *pn* homojunctions.

The diodes used in this study were grown by metalorganic chemical vapor deposition (MOCVD) in a commercial five-wafer reactor. The same reactor and growth procedure has recently produced *p/n* heteroface solar cells which have the highest reported AM1.5 efficiency, indicating very high film quality.[9] The device structure and relevant device parameters are shown in Fig. 1. After film growth, metal
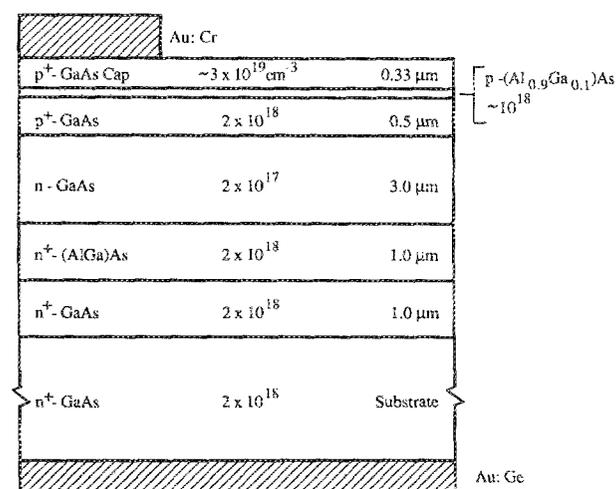

FIG. 1. Cross section of the GaAs diodes used in this study.

patterns were defined using image reversal photolithography and lift-off. Then conventional photolithography and wet chemical etching were used to define mesas. Two size devices were fabricated, one a 0.5 cm on a side square and the second a 0.5 cm by 310 μm rectangle.

The chemical treatments started by etching the devices for 10 s in 1:1:500 H_2SO_4:H_2O_2:H_2O, followed by a rinse in de-ionized water. The Na_2S treatment then consisted of soaking the wafer in a 1 M solution of the sulfide. The device was allowed to soak for up to 10 min to allow for chemical reaction. The devices were then spun dry at 5000 rpm for 60 s, which left a thin polycrystalline film of $Na_2S \cdot 9H_2O$ over the surface of the wafer. If insufficient time (approximately 7 min or less) was allowed for the chemical to react, no surface passivation took place and no reduction of edge currents was observed. Such devices, however, exhibited a hysteresis in their I-V characteristics indicating a charge trapping at the improperly treated surface.

The $(NH_4)_2S$ treatment consisted of making a saturated solution of $(NH_4)_2S$ from H_2S and electronic grade NH_4OH. After etching the sample for 10 s in the 1:1:500 H_2SO_4:H_2O_2:H_2O solution, the wafer was rinsed in de-ionized water and soaked in the $(NH_4)_2S$ solution for up to 5 min. The wafer was then rinsed with de-ionized water and blown dry with N_2. This treatment left no visible film on the wafer.

Displayed in Fig. 2 is a typical diode I-V characteristic before treatment and after the above described Na_2S and $(NH_4)_2S$ chemical treatments. The Na_2S treatment was removed by rinsing in de-ionized water[5] before performing the $(NH_4)_2S$ chemical treatment. [I-V characteristics similar to those shown in Fig. 2 were obtained when the order of the Na_2S and $(NH_4)_2S$ chemical treatments was reversed. The $(NH_4)_2S$ treatment can be removed by spinning on AZ1350J photoresist and then rinsing off the photoresist

FIG. 2. Typical current-voltage characteristics for 1.55×10^{-2} cm^2 devices. The solid line is the initial untreated device, the dotted line is after Na_2S treatments, and the dashed line is after removal of the Na_2S and subsequent $(NH_4)_2S$ treatment. The I-V curves were all measured at 22.2 °C.

with acetone.] As is readily visible, the device initially exhibited no kT diffusion current but only a $2kT$ recombination current (series resistance effects are observed at high bias). After the Na_2S treatment, the device exhibits lower $2kT$ recombination current and a shunt leakage at low forward bias. As also seen in Fig. 2, after the $(NH_4)_2S$ treatment the device exhibited a slightly better reduction in the $2kT$ recombination current than after the Na_2S treatment. In addition, after the $(NH_4)_2S$ treatment the device has one order of magnitude less shunt leakage at low forward bias than after the Na_2S treatment.

We have also observed a much slower aging of our $(NH_4)_2S$ treated devices than our Na_2S treated devices. The cause of the aging of the Na_2S treatment is probably the humidity of the room air since the Na_2S treatment can be removed by rinsing with de-ionized water.[5] Since the $(NH_4)_2S$ passivation persists after the de-ionized water rinse, it is not surprising that the $(NH_4)_2S$ treatment is less reactive with room air.

The expression for the pre-exponential factor for the recombination current is

$$I_{02} = AJ_{02B} + PJ_{02P}, \tag{2}$$

where A and P are the area and perimeter of the device, respectively. Since I_{02} is the measured current, it will contain a bulk component and perimeter component. To quantify the reduction in the surface component, the bulk component must be known. However, to investigate extreme cases where surface or bulk currents are dominating, one needs only to examine the scaling of the current. If the devices are bulk dominated, the ratio of currents for two different size devices will be equal to the ratio of their areas. If the devices are surface dominated, then the ratio of their currents will be equal to the ratio of their perimeters.

The average observed initial I_{02} for our large area devices was 1.76 pA and for our small area devices was 0.931 pA. The ratio of these currents is 1.89. A comparison of this to the ratio of the perimeters (1.88) and areas (16) indicates that the devices are perimeter dominated. Since the initial $2kT$ current is all perimeter current, the perimeter recombination current density is $J_{02P} = 8.80 \times 10^{-13}$ A/cm. For the treated devices, the average values of I_{02} were 1.02 and 0.325 pA for the large and small area devices, respectively. This gives a ratio of 3.14 for the currents, indicating that the devices are neither perimeter nor bulk dominated. However, the surface component has been reduced to a value comparable with the bulk component. We have used Eq. (2) to estimate the $2kT$ recombination current densities after the chemical treatments obtaining $J_{02B} = 1.85 \times 10^{-12}$ A/cm^2 and $J_{02P} = 2.79 \times 10^{-13}$ A/cm. The treatments therefore produced a reduction by a factor of 3.2 in perimeter current.

In conclusion, we have investigated the effects of Na_2S and $(NH_4)_2S$ chemical passivation on the dark I-V characteristics of GaAs pn homojunction diodes. Comparable reduction in $2kT$ edge recombination current by a factor of 3.2 was observed for Na_2S and $(NH_4)_2S$ chemically passivated diodes. The shunt leakage observed at low forward biases for Na_2S treated diodes was virtually eliminated with the $(NH_4)_2S$ surface passivation. We have also demonstrated that even for large area pn GaAs homojunction diodes
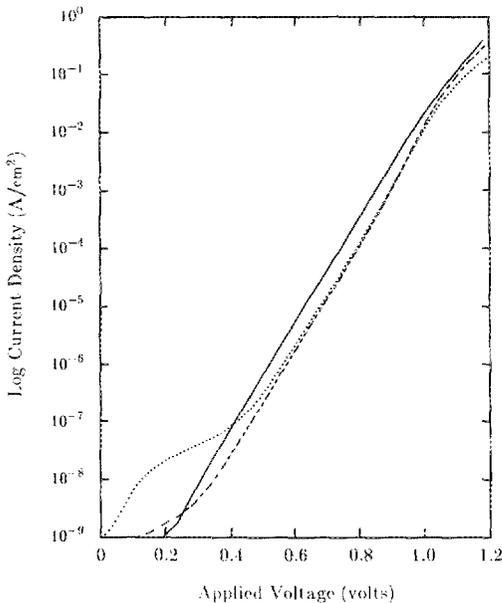
$(A = 0.25 \text{ cm}^2)$, the recombination current is due to edge effects in high quality material.

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