



AUSTRALIAN NUCLEAR SCIENCE & TECHNOLOGY ORGANISATION
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SURFACE PASSIVATION OF
LIQUID PHASE EPITAXIAL GaAs

by

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ABSTRACT

Passivation of the liquid phase epitaxial GaAs surface was attempted using aqueous P_2S_5 - NH_4OH , $(NH_4)_2S_x$ and plasma nitrogenation and hydrogenation. Results indicate that plasma nitrogenation with pretreatment of plasma hydrogenation produced consistent reduction in reverse leakage current at room temperature for all p and n type Schottky diodes. Some diodes showed an order of magnitude improvement in current density. $(NH_4)_2S_x$ passivation also resulted in improved I-V characteristics, though the long term stability of this passivation is questionable.

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KEYWORDS: gallium arsenide, liquid phase epitaxy, passivation, atomic hydrogenation, atomic nitrogenation, plasma, surface treatment, ammonium sulphide.

EDITORIAL NOTE

From 27 April 1987, the Australian Atomic Energy Commission (AAEC) is replaced by Australian Nuclear Science and Technology Organisation (ANSTO). Serial numbers for reports with an issue date after April 1987 have the prefix ANSTO with no change of the symbol (E, M, S or C) or numbering sequence.

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1. INTRODUCTION

Surface passivation is an important means of reducing currents for GaAs devices. This can be understood by examining the transport mechanism of a p-n junction under reverse bias. The leakage current I_R of a reverse biased junction can be expressed as a sum of six current components:

$$I_R = I_d + I_{gb} + I_{gs} + I_{AV} + I_p + I_t$$

where I_d = diffusion current
 I_{gb} = bulk generation - recombination current
 I_{gs} = surface generation - recombination current
 I_{AV} = surface exchange current
 I_p = current through the passivant
 I_t = tunnel current through the passivant

The current component I_d is proportional to the minority-carrier density outside the depletion region and should remain constant for applied bias V_R greater than a few kT . Its temperature dependence should show an activation energy E_a that equals the bandgap E_g of the semiconductor material. The currents I_{gb} and I_{gs} are proportional to their respective depletion widths and, therefore, have a weak V_R dependence of $V_R^{-1/3}$ to $V_R^{-1/2}$ for a diffused junction. I_{AV} depends on the region near the junction and will depend on the level of interface state densities. Currents I_{gs} and I_{AV} can be altered by surface passivation; ideally, the passivant must be such that it will produce flat band conditions. I_p and I_t are also affected by the surface passivation.

Current I_p should be negligible for high resistance passivants. The tunnelling current (I_t) must depend on V_R . Tunnelling can also occur through a combination of thermal excitation and field emission through gap states. The activation energy will then depend on the energy distribution of the gap states; it will be higher for transitions that are mostly through deep states than those that are mostly through shallow states. Under reverse bias, electrons and generation-recombination centres can tunnel out to the conduction band of the semiconductor material, but cannot go to the conduction band of the passivant because of the higher energy required.

Experimental liquid phase epitaxial (LPE) GaAs radiation detectors (diodes) described by Alexiev and Butcher [1], showed in general poor V_R versus I_R characteristics. As often is the case, such characteristics are determined by the surface state densities (due to I_{gs}), impurities such as salt left after the rinse in deionised water, or by surface damage caused by earlier shaping and polishing of the crystal; not least is the surface discontinuity itself giving rise to dangling bonds. There is an obvious appeal in finding a chemical solution to such a problem, in particular, atomic hydrogenation of the surface. However, surface states, although arising from the breaking of specific bonds are delocalised over several atomic layers implying that even though a passivant may complete a bond, optimisation of the passivant species may be required.

In GaAs the root cause of poor electronic surfaces [2] is the high density of surface states formed by segregated arsenic atoms [3] through an oxidation reaction. This results in the Fermi level at the GaAs (100) surface being "pinned" at 0.8 eV below the conduction band.

About 10^{13} states cm^{-2} are involved [2] and several nonstoichiometric phases are present, some of which are conducting [4]. These phases consist of As_2O_3 and Ga_2O_3 , As_2O_3 will be unstable because it reacts with Ga (in the vicinity of the arsenic oxide) by gradually extracting oxygen to form Ga_2O_3 , leading to As segregation [5,6] via the solid state reaction



To counteract this process, Lee et al [7] suggest that a successful passivant must be a species that makes the surface repel approaching oxygen and at the same time have a higher heat of oxide formation than that of gallium oxide. A further requirement must be that the selected species adsorbs strongly on the GaAs (100) surface as an impenetrable barrier. Such species, proposed by Lee et al., are phosphorous compounds. Lee et al. selected in part P_2S_5 , it has a higher heat of formation than gallium oxide and forms an impenetrable barrier to approaching oxygen.

Other efficient surface passivation techniques rely on a reaction between sulphides and the GaAs surface. These reactions form passivating sulphide layers which grow only when the oxide is stripped from the GaAs surface. Sandroff et al. [8] also note that band bending on such a sulphide terminated surface is reduced to 0.12 eV. Similar results have been reported by Carpenter et al. [9], Cowens et al. [10] and Lee et al. [7]. Sandroff et al. [8] notes the surface improvement gained when using $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ persists only for a few days before reverting to its original state. However, Carpenter et al. [9] found that Schottky barriers formed on ammonium sulphide $(\text{NH}_4)_2\text{S}$ treated n and p type GaAs showed no apparent aging after several months exposure to room air. Surface state density was reduced by an order of magnitude when compared to untreated GaAs. Fan et al. [11] reported attaining an interface density of about $1.2 \times 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ for $(\text{NH}_4)_2\text{S}_x$ treated surfaces.

GaAs surface preparation usually follows a similar approach: ultrasonic cleaning in an organic solvent followed by an alkaline etch, typically $\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 3:2:95$ at 40°C for about 30 sec. Samples are then immediately treated with $(\text{NH}_4)_2\text{S}_x$ or $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$.

Other approaches to GaAs surface passivation [12-14] involved exposing the surface to flowing water and light in a photowash cell. This succeeded in unpinning or pinning the Fermi level as the oxygen content of the water was altered; when the water was saturated with hydrogen, large periods of band flattening were noted. The introduction by Ives et al. [12,13] of molecular species of hydrogen into the photowash suggest that some ionic bonding to the arsenic atom may occur with the following reaction:



which implies the formation of Ga-OH and As-H bonds. Such As-H bonds have been reported by Landesman et al. [15] when the GaAs surface is exposed to atomic hydrogen produced by a hydrogen plasma.

Plasma hydrogenation of GaAs defects, impurities and a number of deep centres have been studied over the past ten years [16-19]. Shallow donors and acceptors and a number of deep centres can be passivated by atomic hydrogen and generally their electrical activity can be restored at higher temperatures. However, only little attention was paid to passivating the GaAs surface or the metal-surface interface with atomic hydrogen. First to publish such

investigations was Callegari et al. [20]; they found, after atomic hydrogenation of metal-oxide-semiconductor (MOS) capacitors, improvements in high-frequency response and C-V characteristics. Interface state density was reduced to about $10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ with longer term stability. Paccagnetta et al. [21] applied a similar process to Schottky diodes finding an improvement in the rectifying properties with possible passivation of donors and bulk defects. However, only a partial reduction of the surface state density was noted, implying a partial Fermi level unpinning. The reason for such a poor surface passivation result can be found in a report by Omeljanovsky et al. [22] which observes that RF (tens kHz to tens Mhz) generated atomic hydrogen species has the disadvantage of non-resonant interaction in the RF electric field with charged particles, consequently a low concentration of atomic hydrogen is produced. Their approach was to use a microwave (MCW) plasma source with a resonant magnetic plasma holding capacity [23]. The ionised hydrogen density was found to be two orders of magnitude higher ($\sim 10^{12} \text{ cm}^{-3}$) than a conventional RF plasma. Omeljanovsky et al. (their figures 12 and 13) achieved highly impressive I-V characteristics for hydrogenated Au barrier n-type GaAs Schottky diodes and a two order reduction in surface state density ($\sim 10^{10} \text{ cm}^{-2} \cdot \text{eV}^{-1}$). This suggests that the results of Paccagnella et al. could have been better had the RF induced atomic hydrogen (H) species been at a higher density. On the other hand, a high RF induced H density could also produce surface damage due to sputtering as a result of an increased hydrogen ion (H^+) density, the ratio of H^+ to H depends on the generation frequency and power input [24]. Consequently, low levels of H are produced for passivation at the relatively low generation frequency of an RF plasma.

2. EXPERIMENTAL

2.1 Hydrogen Plasma (RF) Passivation

Even though Omeljanovsky et al. indicate that an RF hydrogen plasma has some inherent disadvantages for GaAs surface passivation, a limited set of experiments were performed using RF plasma. To achieve this a simple arrangement, using an 800 watt 27.5 MHz RF generator, was developed as shown in Fig. 1. Briefly, molecular hydrogen is supplied from a palladium diffuser into a silica column containing a heater pedestal topped with a CZ GaAs wafer which is used to hold and heat the LPE GaAs test samples. The CZ wafer and heater pedestal is shrouded with a silica tube to avoid sputtering contamination back onto the samples. A partial pressure of H_2 was maintained with a vacuum system consisting of a rotary pump, a 120 l s^{-1} turbo molecular pump and a throttle valve located just below the heater pedestal. The heater can be controlled from ambient to 400°C using a simple ON-OFF type controller, so chosen to be immune to RF interference.

All samples, about 5 mm square, were cleaned in an organic solvent followed by a 30 sec etch in $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 3:1:1$ at 60°C . After rinsing in deionised water, the samples were immediately loaded onto the heater pedestal for atomic hydrogenation. The hydrogen plasma was maintained about 6 cm above the sample surfaces and at no time was it allowed to strike the surface. Sample temperatures used were 25°C , 175°C and 270°C . I-V and C-V measurements were done before and after hydrogen plasma exposure following standard metallisation.

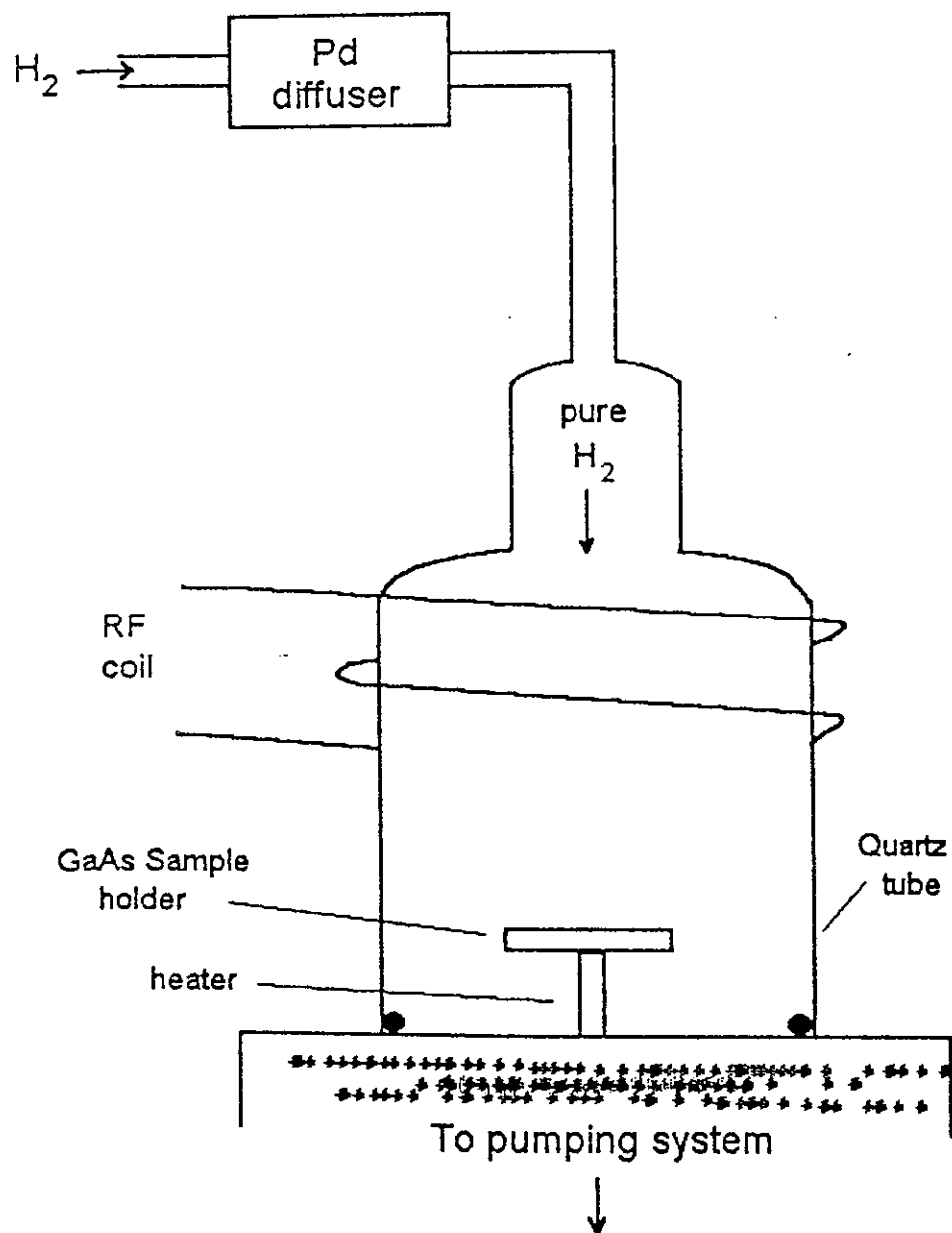


Fig. 1 - Schematic of RF hydrogen plasma source.

Typically, before hydrogenation, such diodes displayed poor leakage currents. Leakage current activation energies were in the order of 0.75 to 0.8 eV, indicative of surface currents, and considerably less than the ideal value of 1.43 eV for bulk conduction. Exposure to atomic hydrogen produced an improvement only when the samples were heated at 270°C and exposed for 2 hours to the plasma. However, some samples showed no change at all. Those that did improve with hydrogenation (typically as shown in Fig. 2) were found to revert after a few days to their original leakage current, suggesting that the GaAs surface was only partially passivated and that the Fermi level reverted to a pinned mid band position. These results confirm the comments of Omeljenovsky et al. on the suitability of RF plasma hydrogenation for surface passivation.

2.2 Nitrogen Plasma (RF) Passivation

The usefulness of atomic hydrogen passivation of the (100) LPE-GaAs surface when the plasma is generated by RF has been found to produce only a marginal effect. However, when pretreating the GaAs surface with atomic hydrogen as described by Pearton et al. [25] and Callegari et al. [20] excess As which can be present either in elemental form or as an oxide As_2O_3 can be removed by the reaction:



Then, without further exposing the surface to oxidation, the excess Ga surface can be altered to form GaN a wide band gap ($E_g = 3.5$ eV) semiconductor layer.

The experimental approach was similar to that used for hydrogen passivation. Briefly, each p and n type LPE GaAs section was etched in $H_2SO_4 : H_2O_2 : H_2O = 3:1:1$ for 30 sec at 60°C, exposed to atomic hydrogen for approximately 0.5 hours followed by 2 hours exposure to atomic nitrogen. Sample temperatures were room temperature to 200°C for hydrogen and up to 360°C during nitrogen treatment. After passivation all samples were metallised to form Schottky diodes and examined using standard characterisation techniques (I-V and C-V).

Results indicate that all p and n type Schottky diodes treated in this manner show a consistent reduction in leakage currents at room temperature with some diodes showing an order of magnitude improvement. The leakage current activation energy also increased, from 0.6 eV to approximately 1 eV. Fig. 3 shows the reverse current characteristic of an untreated sample and the same sample after treatment with the nitrogen RF plasma.

3. AQUEOUS PASSIVATION

3.1 The Aqueous P_2S_5 - NH_4OH Surface Passivant

Lee et al. [7] claim that, when an n-type (100) GaAs surface is exposed to a solution of PCl_3 or P_2S_5 in NH_4OH , a fivefold increase in the photoluminescence can result, together with an improved current - voltage characteristic when the passivated sample is examined with an electrochemical Schottky contact. No other standard characterisation techniques were used. It is therefore of interest to repeat their experiment and examine Schottky diodes prepared with conventional techniques on such surfaces.

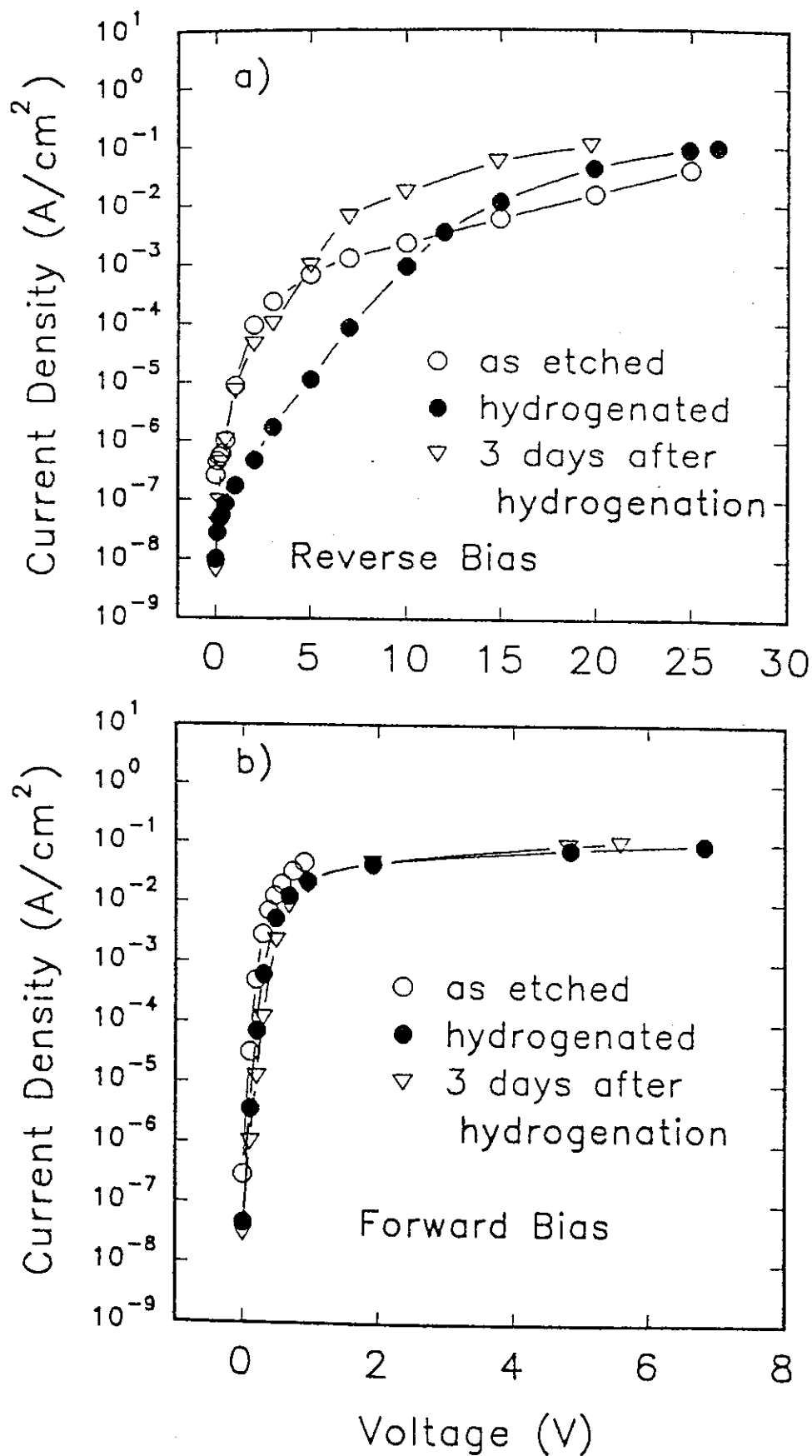


Fig. 2 - I-V characteristics of hydrogenated LPE GaAs sample showing a marginal improvement to the reverse bias current compared to the as-etched sample.

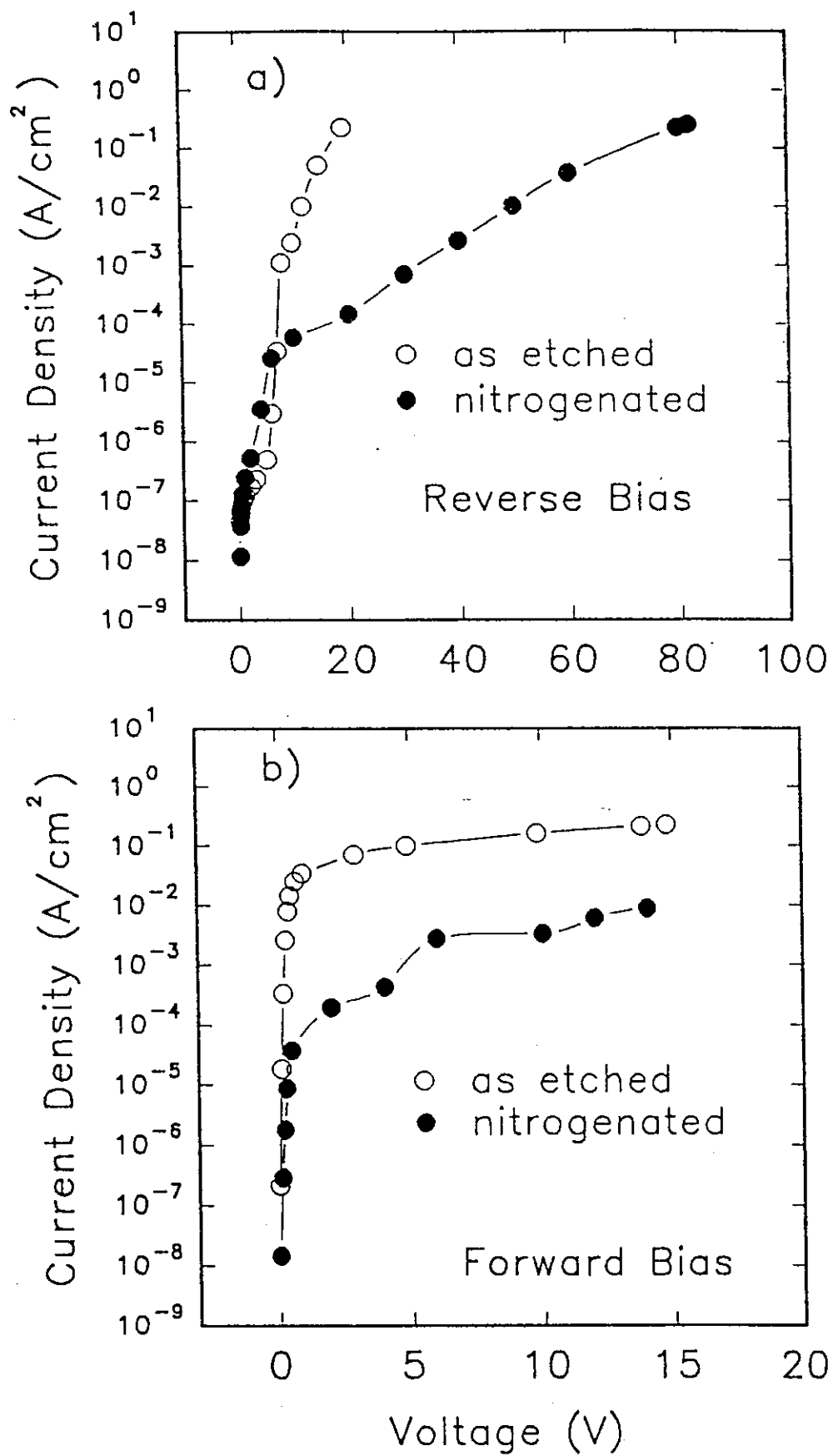


Fig. 3 - I-V characteristics of nitrogen LPE GaAs sample with a substantial improvement in the reverse bias current.

The experimental procedures were as follows:

Samples used were both n and p type, low 10^{14} cm^{-3} carrier density (100) LPE GaAs. The samples were cleaned in organic solvent and rinsed in methanol and deionised ($18\text{M}\Omega\cdot\text{cm}$) water.

This was followed by a sequential series of alkaline based etchants:

$\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 2:2:95$; 4 min at about 40°C ;

$\text{NH}_4\text{OH} : \text{H}_2\text{O} = 1:2$; 1 min at room temperature, used to remove a mixture of lower oxides left after the previous etch;

$\text{HNO}_3 : \text{H}_2\text{O} = 1:19$; 1 min at room temperature, used to remove elemental surface arsenic.

Finally, the samples were placed into the passivant solution:

$\text{P}_2\text{S}_5 : \text{NH}_4\text{OH} = 0.1 \text{ g/ml}$ at room temperature for various times.

After the final step, the samples were removed, dried with nitrogen and metallised in the normal way. All samples were then subjected to I-V measurements and C-V profiling.

Results obtained show that all devices, p or n type, resulted in higher reverse bias leakage currents and an ohmic characteristic (Fig. 4). When plotting $1/C^2$ versus V (Fig. 5), a clear reduction of barrier height from about 0.75 eV to near zero was noted. An attempt to affect the P_2S_5 treated surface by stripping any ionic bound species such as SO_3^- , SO_4^- with a reaction limited etchant ($\text{NH}_4\text{OH} : \text{H}_2\text{O} = 1:100$) did not alter the I-V and C-V characteristics. From the results observed it is clear that $\text{P}_2\text{S}_5/\text{NH}_4\text{OH}$ surface passivation of LPE GaAs is not useful for Schottky diode construction.

3.2 The Aqueous $(\text{NH}_4)_2\text{S}_x$ Passivant

The effects of ammonium sulphide surface treatment of (100) GaAs have been investigated mostly using X-ray photoelectron spectroscopy (XPS) and Raman scattering [8]. This involves comparing the magnitude of two related Raman spectra peaks labelled L^- and LO , corresponding to the degree of optical phonon scattering in the bulk and depleted regions, respectively. Sandroff et al. [8] found that in untreated samples, a high density of surface states lead to a large depletion region and consequently the LO peak appears similar in intensity to the L^- peak. Therefore, the degree of passivation, the reduction of surface state density, lead to a reduction of the LO peak. To find the nature of peak LO , Sandroff et al. used XPS, finding that the GaAs treated with $(\text{NH}_4)_2\text{S}_x$ has complete absence of the characteristic As_2O_3 peak; indicating that the LO peak is directly related to the oxide phase formation on the GaAs surface. The $(\text{NH}_4)_2\text{S}_x$ passivant has been shown to substantially reduce the intensity of peak LO . Carpenter et al. [9] investigated Schottky barrier formation on $(\text{NH}_4)_2\text{S}_x$ treated n and p type GaAs, finding an increase in barrier height and a sensitivity to the metal work function. It is therefore of interest to verify this result by similarly treating LPE-GaAs with $(\text{NH}_4)_2\text{S}_x$, metallising and profiling for I-V and C-V characteristics.

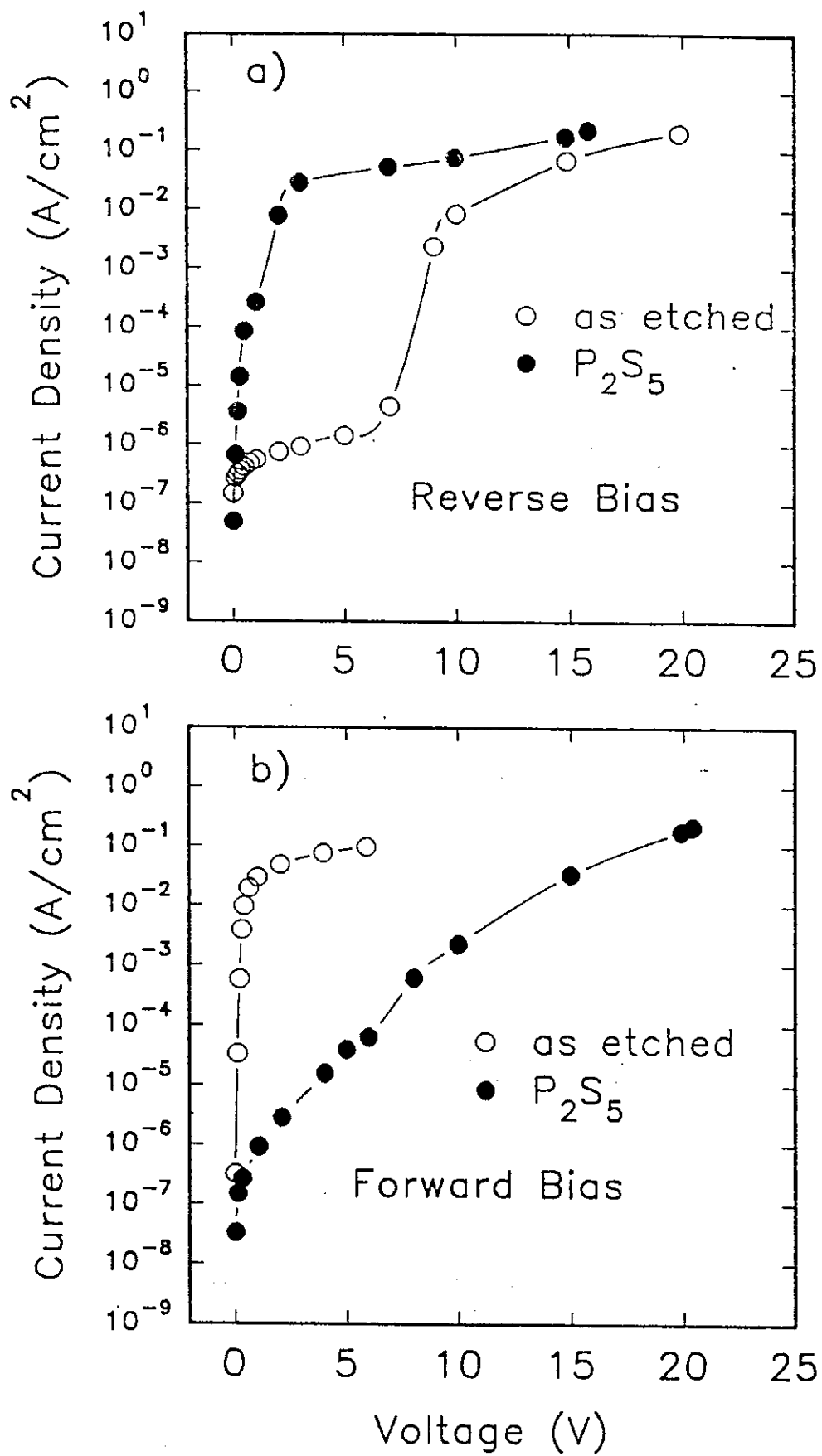


Fig. 4 - I-V characteristics of an LPE GaAs sample passivated with an aqueous P_2S_5 - NH_4OH solution.

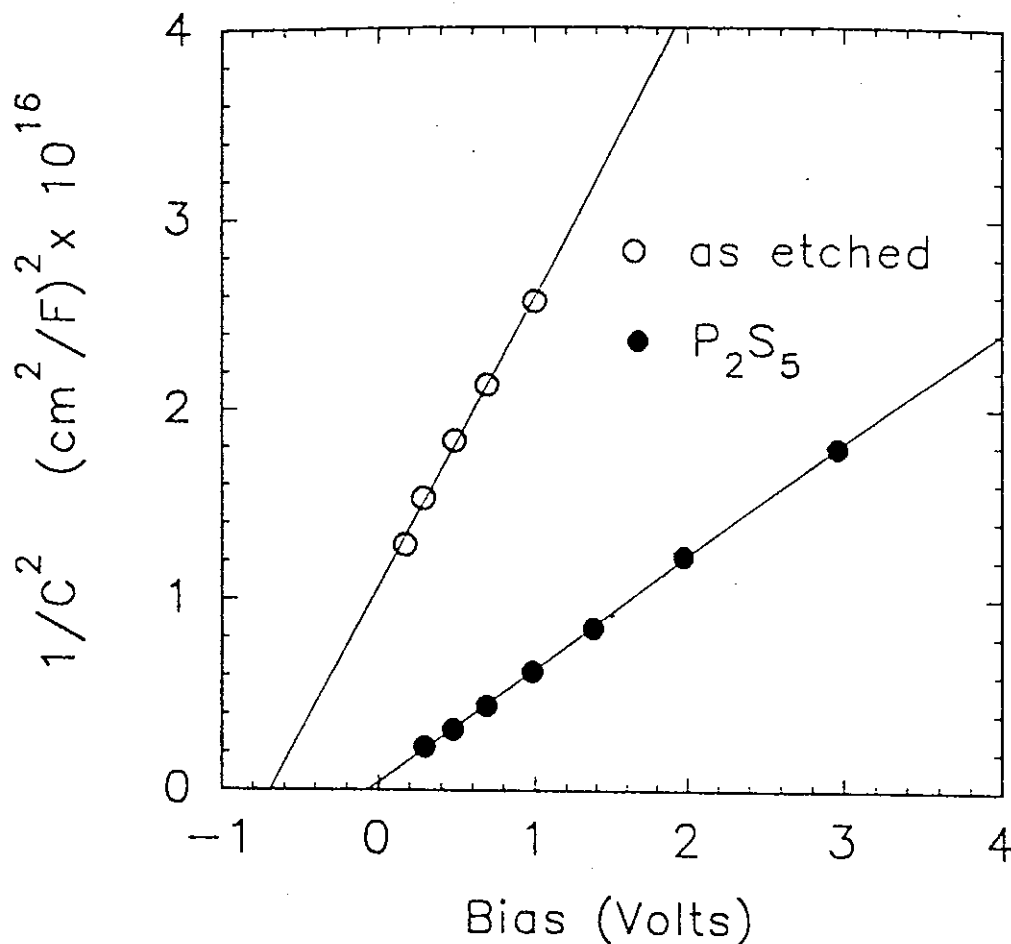


Fig. 5 - $1/C$ versus reverse bias plot for an LPE GaAs sample before and after P_2S_5 - NH_4OH passivation.

The experimental procedure was similar to 3.1, after organic solvent cleaning all samples were etched, firstly in an alkaline based etchant with a second group of samples in a sulphuric based etchant. The GaAs samples were then placed for various time limits up to 5 hours, into the $(NH_4)_2S_x$ solution at $60^\circ C$. Again, after metallisation, I-V and C-V measurements were made. Fig.6 shows a very significant improvement in the reverse current characteristics, C-V measurements confirm an increase in barrier height.

These results for the $(NH_4)_2S_x$ treatment are fairly positive in terms of a passivation treatment which can lower device currents, however, it has been reported that the sulphide layers deposited by this technique are susceptible to oxidation in air particularly when exposed to light [26]. Further work is therefore required to examine and improve the long term stability of this passivation scheme.

4. CONCLUSION

Experimental observations have demonstrated that simple procedures such as nitrogenation and ammonium sulphide passivation can be used to reduce the reverse leakage current of (100) LPE GaAs Schottky diodes. Improvement in the long term stability of the $(NH_4)_2S_x$ passivation is required. RF hydrogen plasma passivation was found to be unstable under conditions which initially improved device currents.

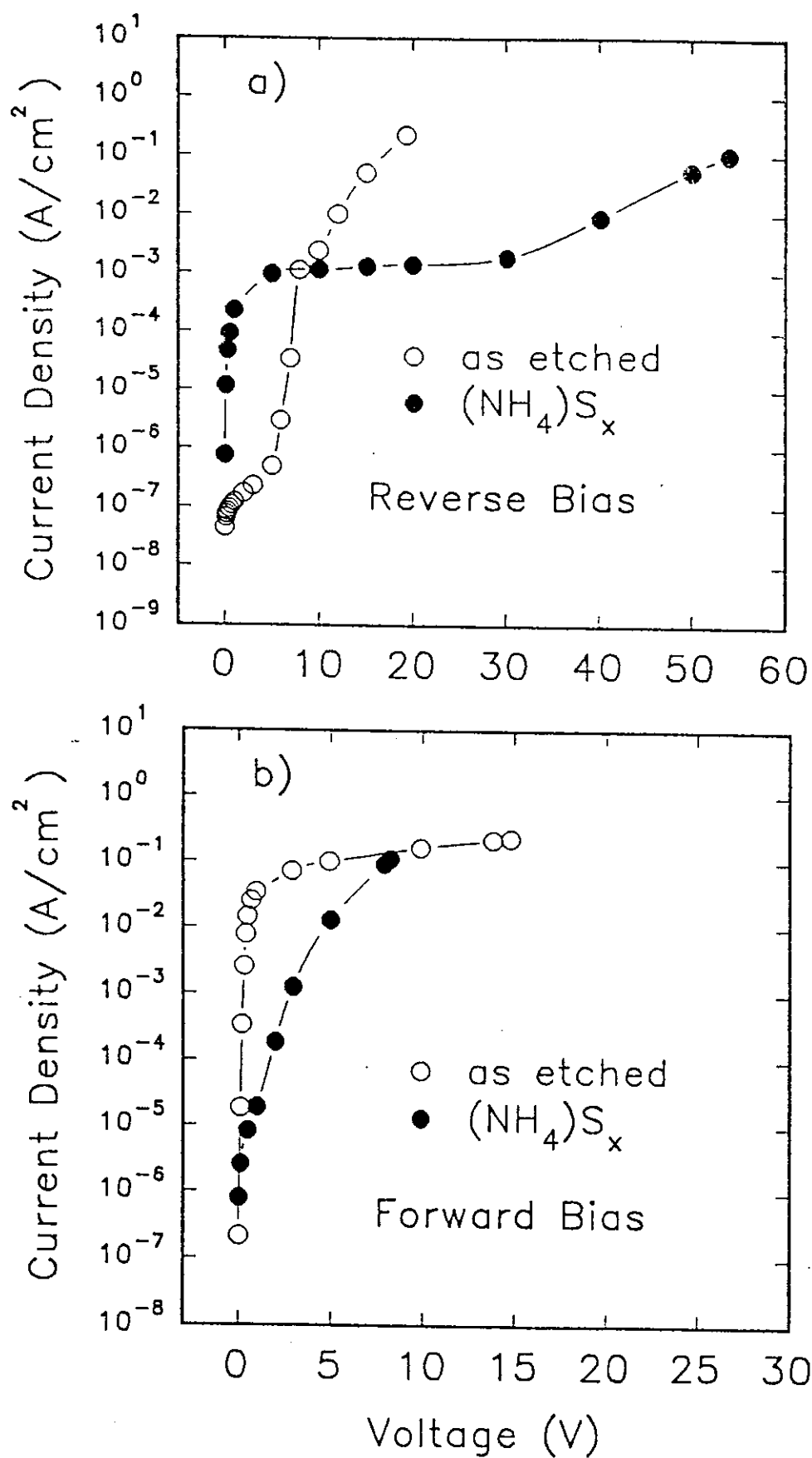


Fig. 6 - I-V characteristics of an LPE GaAs sample passivated with an $(\text{NH}_4)\text{S}_x$ solution.

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