Title

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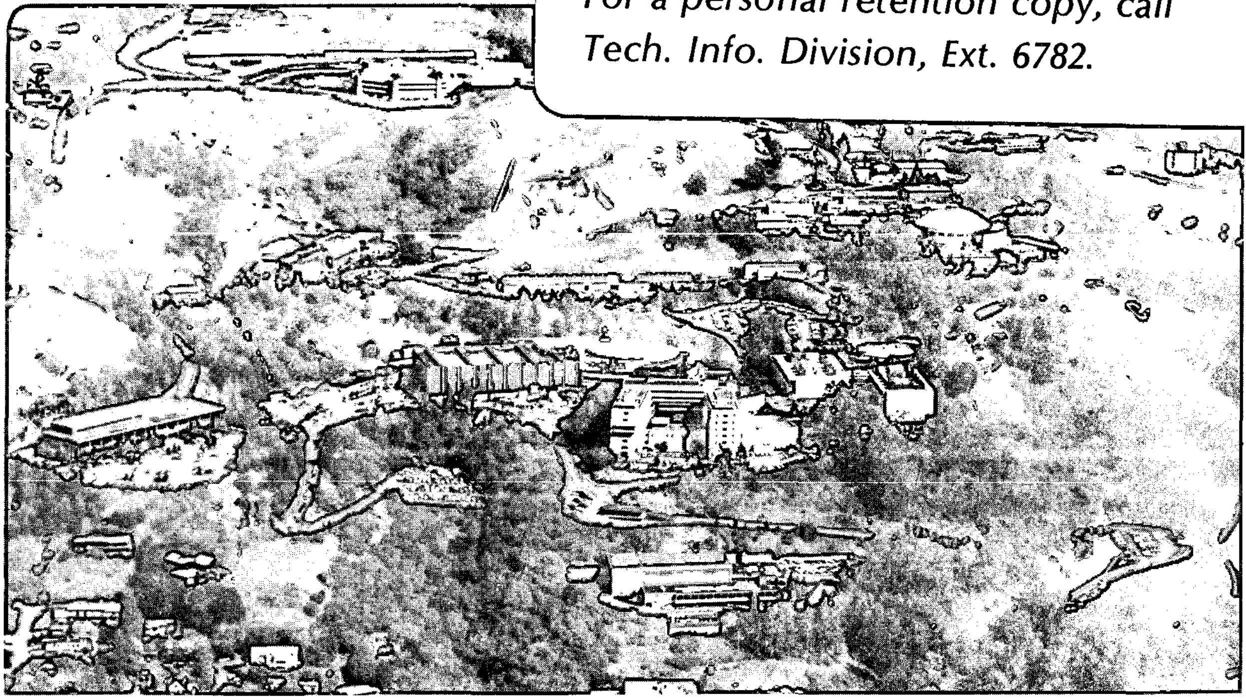

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Nitridization of gallium arsenide surfaces: effects on diode leakage currents

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Nitridization of GaAs surfaces by exposure to a nitrogen or nitrogen-hydrogen plasma is known to form a surface coating rich in GaN. We show that pretreatment in a hydrogen plasma at room temperature followed by production of this wider band gap material by nitrogen plasma treatment at 500°C for 5 h reduces the reverse leakage current of Au-GaAs ($N_D - N_A = 5 \times 10^{17}$ cm^{-3}) Schottky diodes by typically an order of magnitude at 300 K.

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It has recently been shown that exposure of GaAs to a low pressure nitrogen or ammonia plasma can create a surface layer composed of GaN and various arsenic nitrides[1,2]. The formation of this layer has been investigated by reflection electron diffraction, photoemission, photoluminescence and secondary ion mass spectrometry on bulk samples. It has also been suggested that such plasma treatments could be of importance in GaAs device fabrication, particularly in reducing the surface contribution to diode leakage currents[1-3]. Indeed the use of plasma nitridization in the fabrication of MIS structures on GaAs has received attention[4]. Other treatments such as chemisorption[5], have proven successful in reducing surface recombination on GaAs by reacting with excess As. Free As is known to produce deep surface states which act as generation-recombination centers[3]. Pretreatment of the GaAs surface with a hydrogen plasma should remove this excess arsenic, which is present either in elemental form or as As_2O_3, by producing volatile AsH_3. Subsequent treatment in a nitrogen plasma then forms the nitrided layer. Capasso and Williams[3] have further proposed an additional deposition of Si_3N_4 as a stable, long-term surface passivant. We have performed a series of experiments using nitrogen, hydrogen, and nitrogen-hydrogen plasmas to determine the suitability of the nitridization method to Au-GaAs diodes, and the optimum plasma exposure conditions.

Samples from a <100> Si-doped ($N_D - N_A = 5 \times 10^{17}$ cm^{-3}) LEC GaAs crystal[6] were cut into 4 x 4 mm^2 sections, and evaporated AuGe was alloyed to the rear faces at 475°C for 5 min in flowing H_2 gas. The front surfaces were polish etched in $3HNO_3:2H_2O:1HF$ before exposure to a 13.6 MHz, 0.1 Torr plasma of boil-off nitrogen, palladium-diffused hydrogen, or a mixture of the two (~ 1:3 ratio). The samples were mounted on a graphite block within a quartz tube for the plasma exposures, and the temperature of the substrate measured by an optical pyrometer. After plasma treatment at temperatures of 300 - 600°C for periods between 15 - 120 min, all surfaces with the exception of a 2 mm diameter circular section of the top surface were masked, and the GaN on this section etched in $3H_2SO_4:1H_2O_2:2H_2O$. Gold Schottky barriers (400 Å thick) were then evaporated onto this section such that they intersected the nitrided layer. Leakage current measurements were performed over the temperature range 100 - 370°K by installing the samples in a closed-cycle refrigerator-cooled cryostat.

Figure 1 shows the temperature dependence of reverse leakage current for a bare Au-GaAs diode at a reverse bias of 3 V. The characteristic is composed of two distinct regions, with activation energies of 0.74 eV at higher temperatures (>280 K), and 0.60 eV at lower temperatures. Such a characteristic was typical of the diodes fabricated from this material. One would expect the activation energy of the reverse current to equal the band gap of GaAs (1.43 eV) for an ideal, trap free diode. In the presence of deep traps and surface current components Sze[7] has shown that the ideal equation must be modified by reducing the activation energy term by a factor between 1 and 2. An extensive number of plasma types (N, H, N + H, O) and exposure sequences were tried (e.g. nitrogen only or nitrogen followed by hydrogen) to determine the optimum conditions for forming a passivated surface on the GaAs. Figure 1 also shows that simply exposing the GaAs to a H plasma for 0.5 h at 500°C was unsuccessful in producing any passivation, and in fact makes the characteristic considerably worse. This is in agreement with the results of Pankove *et al.*[1] who found no decrease in surface recombination after hydrogenation. We expect that plasma etching of the GaAs[8] will remove most of any surface oxide present before treatment, although Friedel and Gourrier[9] have shown that additional heating at 530°C is needed to completely eliminate oxygen.

Exposure to a H plasma for 10 min at room temperature to clean the surface, followed by treatment in a N plasma at elevated temperatures was consistently successful in reducing the diode leakage current. Figure 1 shows the range of leakage currents measured for samples treated in the N plasma for 0.5 h at 500°C. At room temperature the leakage current of a passivated diode was typically an order of magnitude lower than that of a bare diode. The activation energy of the plots for the plasma treated samples is ~ 1.1 eV, and seems to have only a single slope. Once again, this activation energy is difficult to relate to the band gap of GaN (3.5 eV), as the diode leakage current is composed of both surface and bulk (GaAs) components, and the nitrided layer is a mixture of GaN and various arsenic nitrides. Using the data of Gourrier et al.,[2] we may make a rough estimate of the nitrided layer thickness as being ~ 10 Å.

If the sample was simply heated in a N plasma without first cleaning the surface using the H plasma, variable results were obtained, and in general the diode leakage currents of such samples were worse than the H, N plasma-treated samples. Similarly, exposure of the GaAs to the N plasma at temperatures below ~ 425°C was unsuccessful in producing any significant surface passivation, whereas exposures at temperatures above ~ 550°C produced progressively smaller reductions in leakage current until at ~ 600°C the characteristics were worse than those of the bare diodes. We attribute this to decomposition of the GaAs surface. The greatest degree of surface passivation on the material we used was obtained at ~ 500°C. The temperature of the exposure was the most critical parameter—changing the plasma pressure to 0.5 Torr did not significantly change the results obtained, and extending the exposure time to 2 h also had no consistent effect. The use of a combined N and H plasma produced similar degrees of passivation as a pure N plasma (preceded by the H plasma surface cleaning), but exposure to a N plasma followed by a H plasma was not successful. In general, diodes treated in this manner had higher leakage currents than N or N + H plasma-treated samples. Use of an oxygen plasma either by itself or in sequence with N or H plasmas was never successful in producing surface passivation.

We note that simply heating the samples in molecular nitrogen for the same conditions under which the nitridizations were carried out did not reduce the leakage current of subsequently fabricated diodes. Indeed the leakage currents were invariably worse, due probably to the well-known problem of As outdiffusion leaving a disordered surface. Heating in a H plasma, which is known to passivate bulk electrically active defects in GaAs,[10,11] including the common EL2 centers[12] present in this material, did not lead to reduced leakage currents, ruling out some bulk defect passivation mechanism as the cause of the better diode performance. We therefore believe that the only cause for the observed reduction in reverse biased diode leakage current is the formation of the nitrided surface layer.

Figure 2 displays the room temperature diode characteristics of untreated and nitrided samples, and shows that the N plasma exposed diodes retain their lower reverse leakage currents out to the breakdown voltage. The forward leakage currents of untreated and passivated diodes are not significantly different. We attempted to fabricate the Schottky contact first, and then expose the sample to the plasmas, but alloying of the Au with the GaAs at the elevated temperatures used always led to poor diode performance. Also, evaporation of a gold contact onto a nitrided layer, without first etching the GaN to expose the GaAs gave a device with low leakage current, but a poor rectification ratio, as the nitrided layer is basically insulating.

In conclusion, we demonstrate that plasma nitridization of GaAs surfaces, followed by diode fabrication, results in devices with lower reverse leakage currents than unpassivated diodes. A considerable amount of work remains to be done concerning the effects of the purity of the bare material and the stability of the nitrided layer, but there is at least evidence that this layer is effective in reducing surface leakage currents on GaAs.

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FIGURE CAPTIONS

Fig. 1. Reverse leakage current versus inverse temperature plots for Au-GaAs diodes comparing an untreated sample with diodes fabricated on H-plasma- or N-plasma-exposed samples. Simply heating in a H plasma at 500°C for 0.5 h leads to a worsened characteristic, but nitridization at the same conditions leads to typically an order of magnitude lowering of the leakage current. The hatched area represents the spread of leakage currents obtained after nitridization at 500°C.

Fig. 2. Current-voltage characteristics of Au-GaAs diodes, comparing a bare surface device to a nitrided surface.

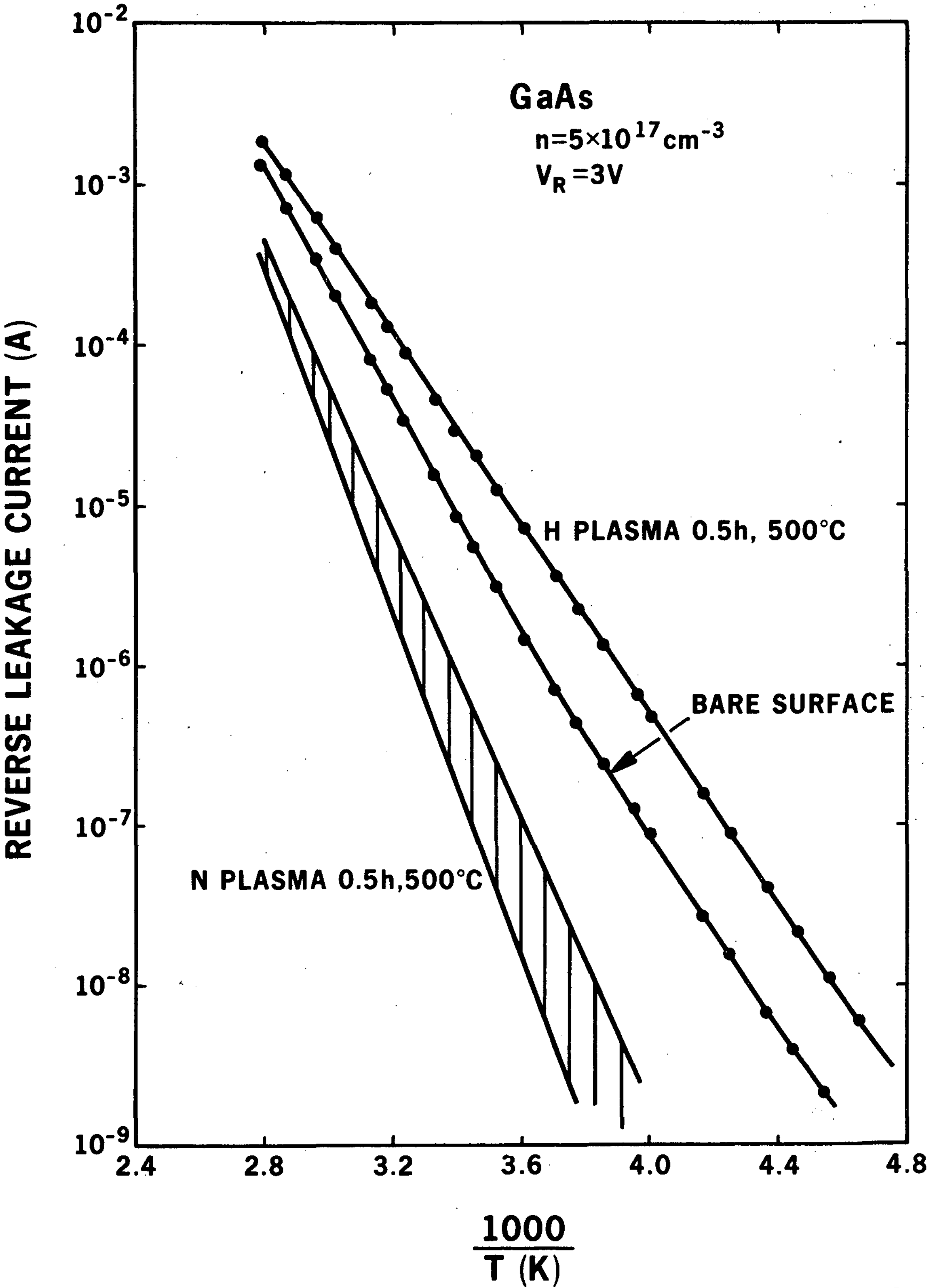

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Fig. 1.

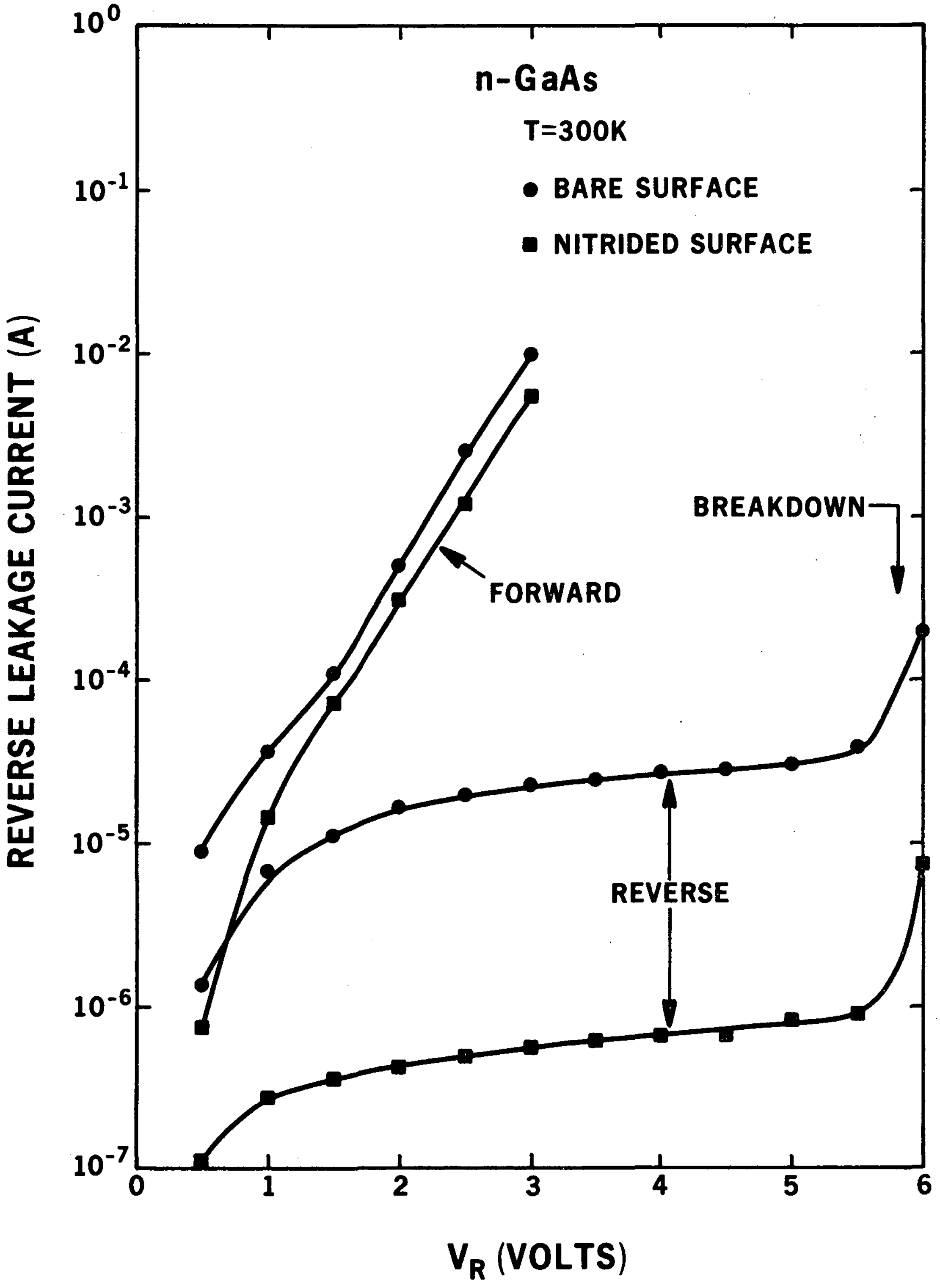

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Fig. 2.

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