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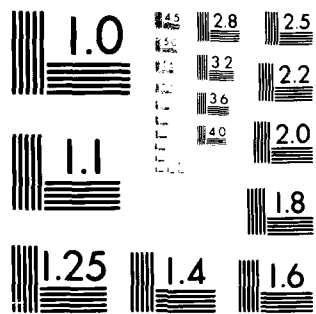   AUG 80 J I PANKOVE   F49620-80-C-0039
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PASSIVATION OF GaAs SURFACES

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Various approaches to passivating the surface of GaAs have been explored. All of these were aimed at tying dangling bonds with atoms bonding more tightly than either Ga or As. Atomic species of hydrogen and nitrogen were generated by a glow discharge in H_2, NH_3, or N_2. Nitridization with ammonia appears most promising. The degree of passivation was monitored by photoluminescence. A fourfold improvement in luminescence efficiency was obtained with nitridization while a factor-of-ten improvement can be obtained with the less practical technique of generating an (AlGa)As skin.

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LIST OF ILLUSTRATIONS

SECTION I

INTRODUCTION

The purpose of this research project is to eliminate surface states and dangling bonds that are responsible for carrier recombination and leakage current in GaAs devices. Surface states and subsurface defects form levels inside the energy gap that act as recombination centers that reduce the lifetime of injected minority carriers. Furthermore, in the presence of an electric field, these centers generate randomly excess electron-hole pairs that contribute undesirable noise.

Our approach to this problem has followed a dual path: (1) to attach selected atoms (hydrogen or nitrogen) to dangling bonds, and (2) to widen the energy gap near the surface, thus creating a potential barrier that repels both electrons and holes away from the surface (Fig. 1).
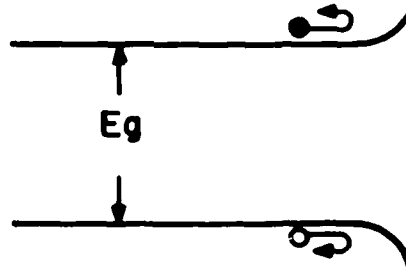
Figure 1. Energy diagram of a passivated system.

A similar problem in crystalline silicon has been successfully resolved by attaching atomic hydrogen to silicon dangling bonds [1]. This caused a dramatic reduction in surface leakage current by eliminating the corresponding recombination centers. Furthermore, since the Si-H bond is stronger than the Si-Si bond, the energy gap of the hydrogenated material is larger than that of the untreated silicon.

We have attempted to apply similar techniques to GaAs by replacing As or Ga at the surface by an atom having a stronger binding energy. By coating the surface with Al, P, or N, larger-energy gap compounds can be formed: $Al_{1-y}Ga_yAs$, $GaAs_{1-x}P_x$ or $GaAs_{1-x}N_x$. Also, the use of atomic hydrogen was explored, as in the above-mentioned case of silicon.

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Earlier attempts at passivating the surface of GaAs have consisted in coating the crystal with silicon oxide [2] or Si_3N_4 or AlN [3]. SiO_2 had a tendency to blister upon heating, whereas the Si_3N_4 and AlN acted more as encapsulants than as passivants. A high-dose implantation of phosphorus seems to reduce the decomposition of GaAs under the SiO_2 encapsulant during high-temperature annealing [4]. Ge_3N_4 coatings suffer from oxygen contamination [5]. An order-of-magnitude drop in surface recombination has been achieved by a chemical treatment that deposits 0.3 monoatomic layer of ruthenium on GaAs [6]. Effective passivation can be achieved with a layer of wider-gap AlGaAs [7]. However, since AlGaAs is hygroscopic, it is not a reliable passivant for practical device applications.

SECTION II

MATERIAL PREPARATION

A. LIQUID-PHASE EPITAXY OF GaAs

The highest-quality GaAs (high carrier diffusion length) is produced by
liquid-phase epitaxy (LPE) of GaAs on the (100) surface of commercial-grade
GaAs substrate. A multibin boat (shown in Fig. 2) is used. The substrate is
placed in the recessed area in the graphite slide. One bin is filled with Ga
that had been saturated with GaAs at 880°C. The boat is then placed in a
quartz furnace and the temperature is raised to 880°C; the slide is pushed to
position the substrate under the Ga solution; the temperature is raised by one
degree to remove by dissolution the upper layer of the GaAs substrate. Then,
the temperature is lowered to cause the epitaxial deposition of the GaAs that
exceeds the solubility limit at the deposition temperature. Next, the temper-
ature is dropped at the rate of one degree per minute to 860°C. Finally, the
slide is moved to remove the substrate from under the Ga solution, and the
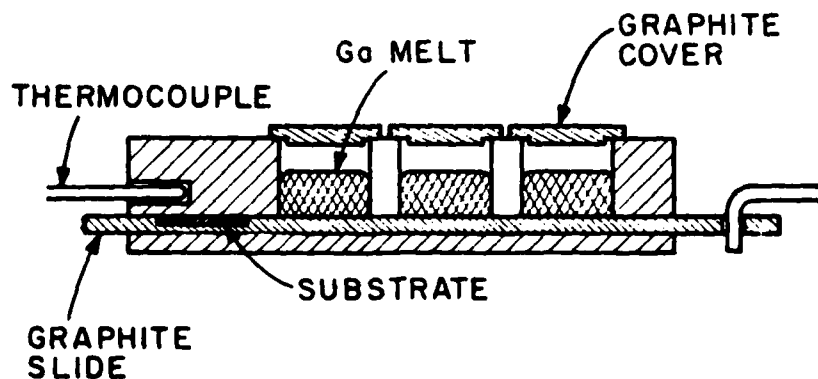furnace is cooled.

Figure 2.   Schematic showing the basic multiple-bin graphite
            boat for the sequential deposition of several layers
            during one growth cycle.

The layer of GaAs produced by LPE, about 10 µm thick, has a mirrorlike smoothness with minor ripples on a microscopic scale. Sometimes a few small droplets of Ga remain on the surface; these are removed with a cotton swab and TCE. A cross section of LPE GaAs on GaAs substrate is shown in Fig. 3.
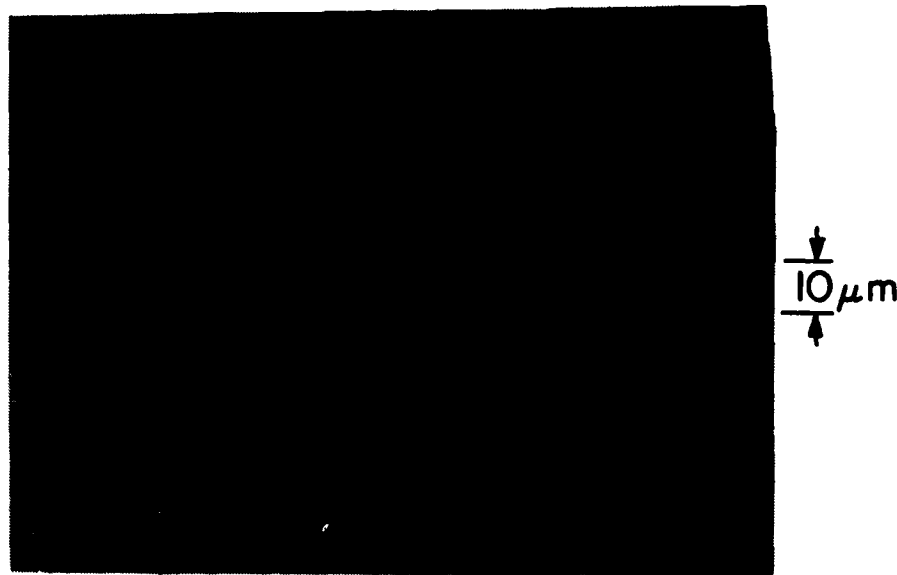
Figure 3. Photomicrograph of a cross section of a typical GaAs specimen.

For the luminescence measurements to be described below, the Ga-GaAs solution was doped with Ge so that the final LPE layer contained a concentration of 2×10^{18} Ge/cm^3. For electrical measurements, where an insulating passivating layer is desired, chromium was used as the doping impurity.

B. HETEROTRANSITION TO (AlGa)As

The standard of comparison for low surface recombination was a heterostructure of (AlGa)As grown epitaxially by LPE on an epitaxial layer of GaAs:Ge produced as described in the above section. The (AlGa)As layer was generated immediately after the GaAs layer (5 µm thick) by moving the substrate to a second bin containing a saturated solution of Al-Ga-As. The temperature was lowered to generate a 0.3-µm-thick layer of $Al_{0.4}Ga_{0.6}As$. This "standard" is kept in a dry box.

C. SURFACE TREATMENTS

The GaAs crystal was cleaved into four or more strips, one of which was kept as an untreated control while the others were processed under different conditions with only one parameter intentionally varied (e.g., temperature).

The GaAs was exposed to atomic ambients at various temperatures in the apparatus shown in Fig. 4. The glass or quartz tube is evacuated before admitting either hydrogen, nitrogen, or ammonia at low pressure . An rf generator capacitively coupled to the gas produces a glow discharge at ∿130 MHz. The collisions between ionized molecules cause their dissociation into the atomic species. The atoms, both neutral and ionized, diffuse down the tube to the GaAs, the temperature of which is controlled by the furnace.
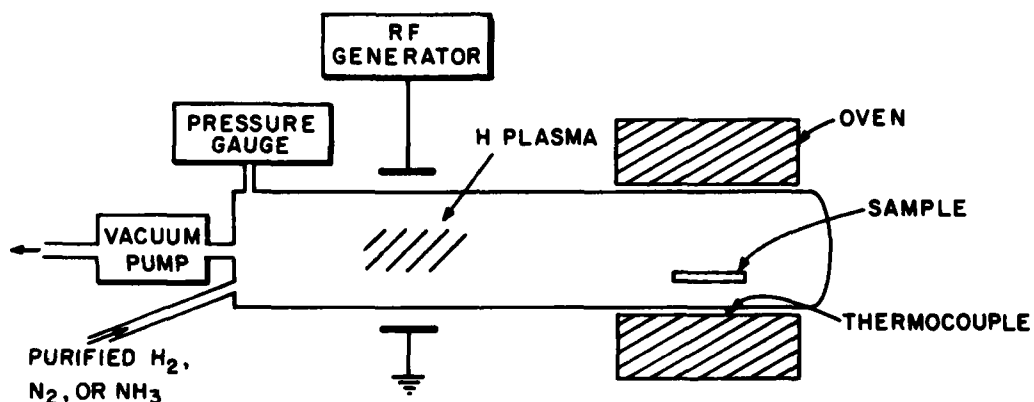
Figure 4. Apparatus for the hydrogenation of semiconductors.

After exposure at the desired temperature for a predetermined time, the sample is rapidly cooled by removing the furnace and substituting an air blower. When the tube is cool to the touch, the plasma is turned off and the sample removed.

The treatment in atomic hydrogen duplicated the earlier experiments with Si. However, a larger range of temperatures was used since we did not know the temperature at which H evolves from GaAs. It was hoped that H would passivate any dangling bond at the surface of GaAs.

The treatment in NH_3 was intended to form a layer of the wider-gap GaN wherever an As vacancy would develop; and it was hoped that hydrogen would passivate any residual dangling bonds.

5

The treatment in nitrogen was attempted to form a layer of GaN on GaAs. In one run, the GaAs was located inside the nitrogen plasma.

D. TEST PROCEDURE

The test for passivation consisted in measuring the photoluminescence of GaAs at room temperature. As shown by Ettenberg and Nuese [8], the luminescence efficiency of GaAs strongly depends on surface recombination (Fig. 5). The sample was excited by the blue light from an argon laser. This produces
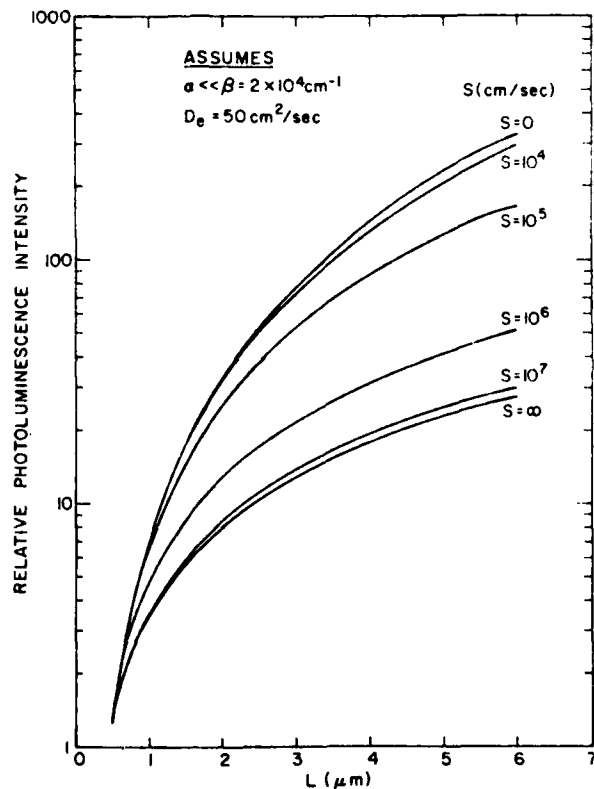

Figure 5. Plot of relative photoluminescence intensity for GaAs vs minority-carrier diffusion length as a function of surface-recombination velocity for an absorption coefficient of the incident radiation equal to 10^5 cm^{-1}.

electron-hole pairs near the surface where they are most susceptible to surface recombination. The radiative recombination of the surviving pairs is detected by a lead sulfide photoconductor cooled to dry-ice temperature. If the surface is passivated, surface recombination is greatly reduced, and the luminescence intensity increases (see Fig. 6). The "standard" with the (AlGa)As heterotransition is our guide for ultimate quality: its luminescence efficiency is ten times greater than that of a bare untreated LPE GaAs:Ge.
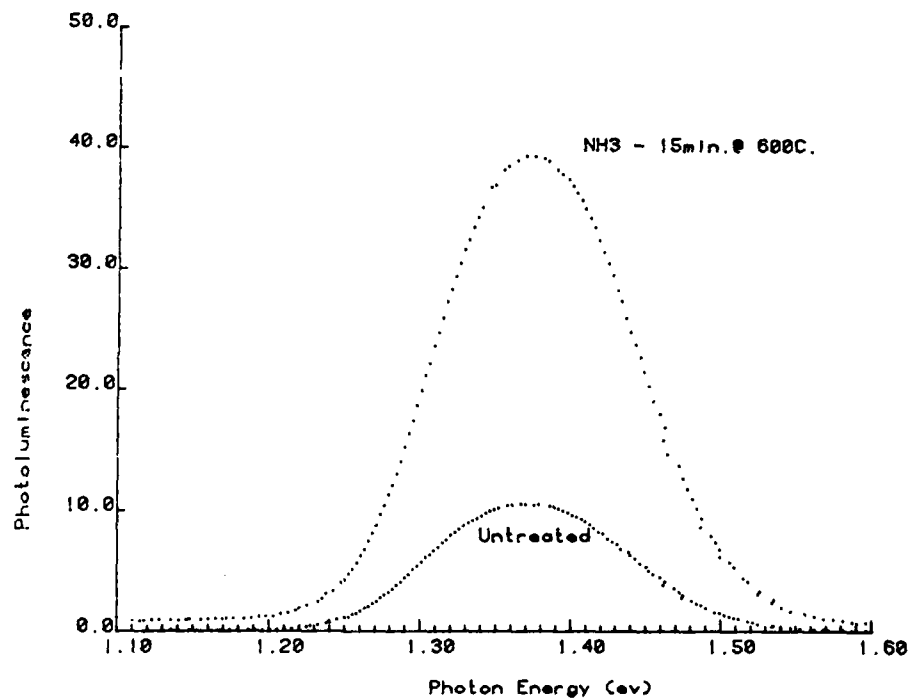
Figure 6. Photoluminescence spectra, at room temperature, of treated and untreated GaAs.

The spectra were recorded on a Tektronix* 4051 computer and processed to print the intensity of emitted light vs photon energy.

*Tektronix Inc., Beaverton, OR.

A. EXPOSURE TO ATOMIC HYDROGEN

Figure 7 shows the effect of exposing GaAs to atomic hydrogen for 1/2 hour at various temperatures ranging from 100 to 660°C. Three pieces of the same crystal were treated four times to explore the full temperature range until dissociation of GaAs caused us to stop any further temperature increment.

Figure 7. Relative photoluminescence of GaAs treated in atomic hydrogen for 1/2 hour at indicated temperatures. Each symbol indicates one of four pieces of the same starting crystal. Three of the pieces were treated four times. The untreated reference piece is symbolized by ▲.

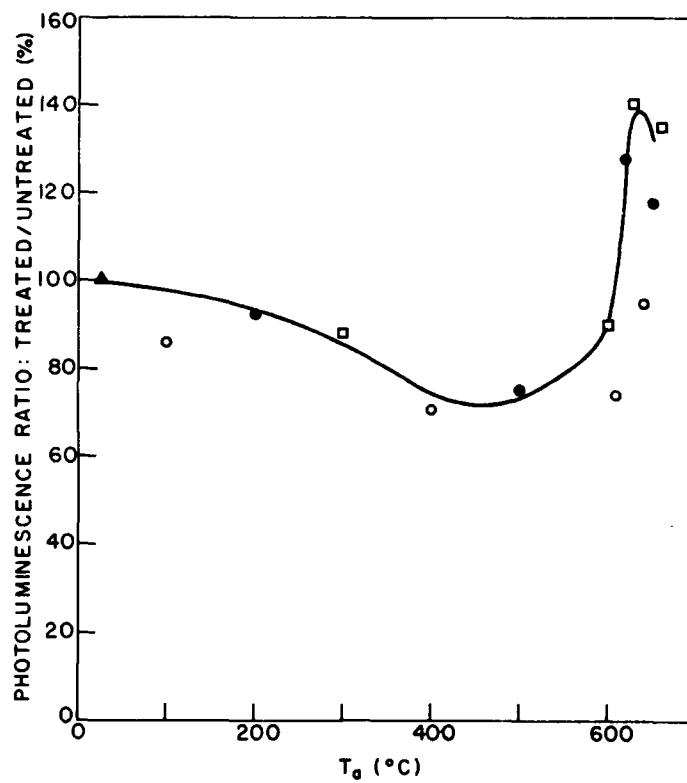After decomposition, the surface was rough and pitted. The increase in luminescence efficiency can be explained in terms of reduced specular reflectance of the GaAs surface: the lower reflectance allows more laser light to enter the crystal and allows more recombination light to escape the GaAs.

B. EXPOSURE TO AMMONIA PLASMA

Figure 8 shows the effect of exposing GaAs to NH_3 plasma for 1/2 hour at various temperatures from 100 to 600°C. A fourfold improvement in luminescence efficiency was obtained at 600°C. The sample appeared to have acquired a transparent glaze which was presumed to be GaN. Further heating at still higher temperatures destroyed these surfaces.
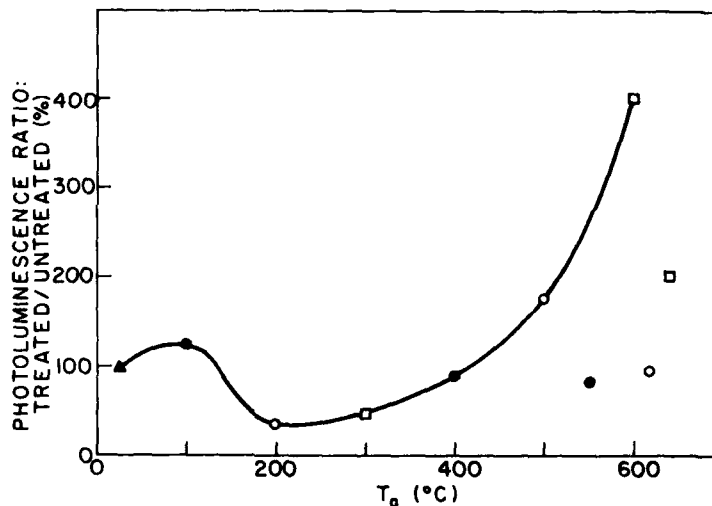
Figure 8. Photoluminescence of GaAs treated in ammonia for 1/2 hour at indicated temperatures. Each symbol indicates one of four pieces of the same starting crystal. Three of the pieces were treated three times.

Another series of treatment with NH_3 plasma at 600°C was done as a function of time to test the hypothesis that there might be an optimum thickness of GaN beyond which nitrogen could not penetrate the GaN while the evolving As would flake away patches of GaN. The data of Fig. 9 suggest that the optimum treatment should last 10 min.

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Figure 9. Luminescence intensity of GaAs treated in
atomic hydrogen at 600°C as a function of
hydrogenation time.

Several additional runs were made for 15 min at various temperatures and
showed that an improvement by a factor of three could be obtained in the 550
to 600°C range (Fig. 10).

Annealing at 575°C with NH_3 plasma as a function of time suggested that a
factor-of-three improvement may be a saturating limit (Fig. 11). However, we
soon discovered that the samples treated with NH_3 plasma suffer from lumines-
cence fatigue: the luminescence efficiency gradually decreases in time in the
area exposed to the laser beam. There is no degradation of the luminescence
efficiency in the nonirradiated regions. Figure 12 shows a scanned lumines-
cence profile along the six strips of the same GaAs wafer. Each strip was
annealed at 600°C for the indicated duration. The drop in the luminescence
profile near the center of each strip results from a 15-min exposure to 50 mW
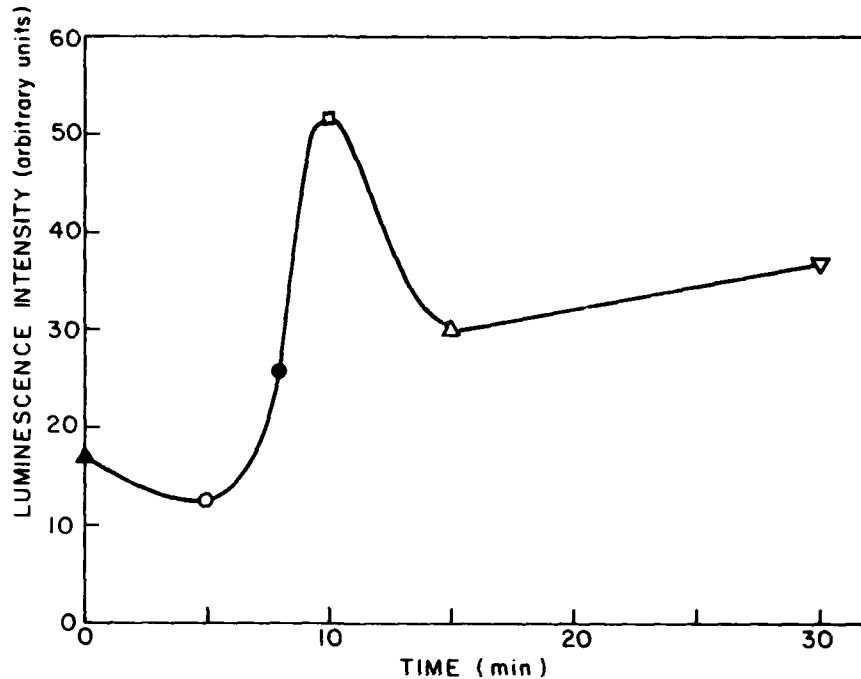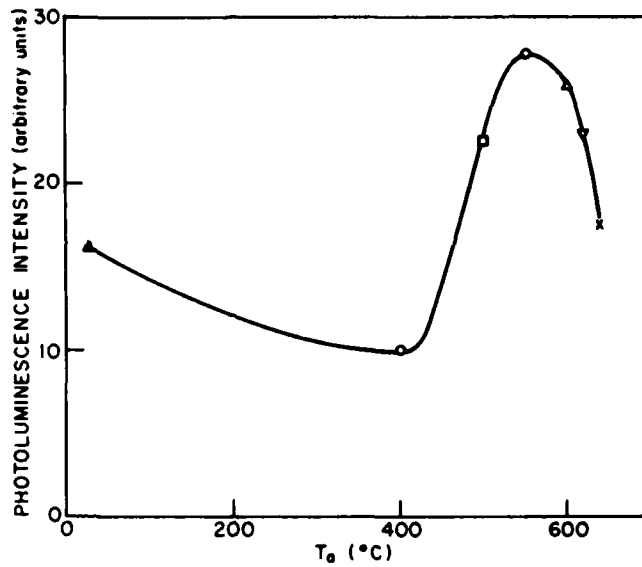
Figure 10. Luminescence intensity of GaAs treated in ammonia
for 15 min as a function of treatment temperature.
Each symbol represents one of seven pieces from
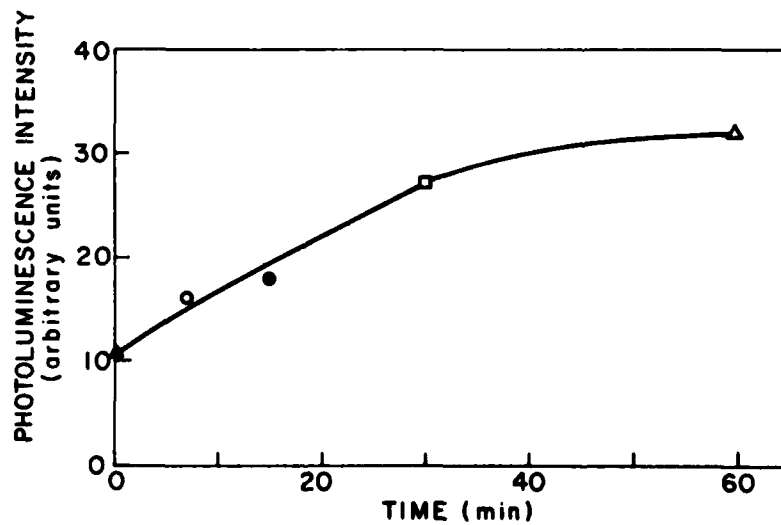the same starting crystal.

Figure 11. Luminescence intensity of GaAs treated in ammonia
plasma at 575°C as a function of treatment time.
Each symbol represents one of five pieces from the
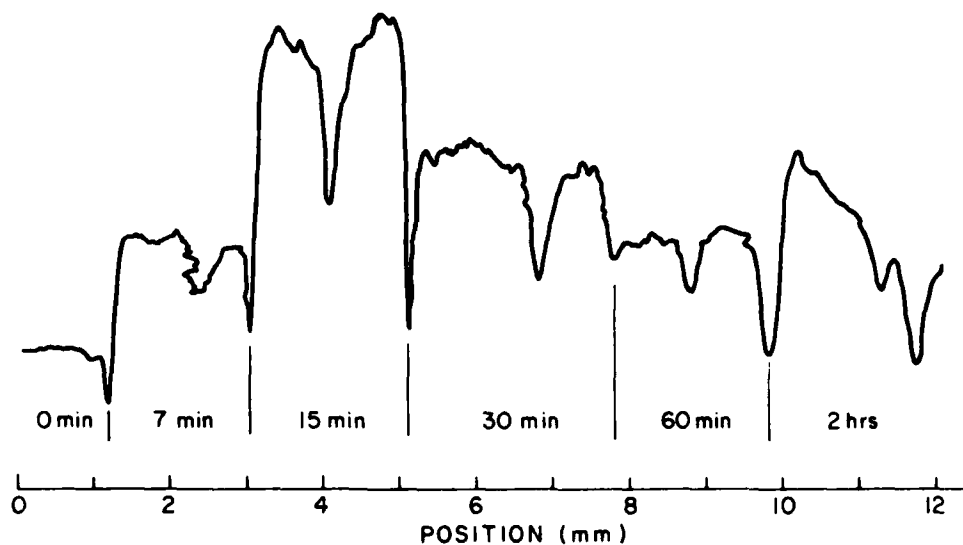same crystal.

11

Figure 12. Luminescence intensity profile of six pieces from the same crystal, each exposed to ammonia at 600°C for the indicated duration. One spot in each piece had been irradiated for the indicated duration with

50 mW at room temperature before measuring the profile.

of laser radiation. Strip #4 was then treated with NH_3 plasma at 600°C for 30 more minutes, and this annealed the light-induced damage of the previously fatigued area (Fig. 13). Then laser irradiation for 15 min at the center of the strip caused a substantial decrease in efficiency. Note that the photo-induced degradation can be large. Further annealing with NH_3 plasma erased the optically induced defects but also depressed the luminescence efficiency, in agreement with the earlier finding that there is an optimum exposure time for the NH_3-plasma treatment.

C. EXPOSURE TO NITROGEN PLASMA

A series of treatments with N_2 plasma for 10 min at temperatures ranging from 575 to 725°C doubled the luminescence intensity. However, an uncertainty of 40°C due to nonuniform temperature distribution in the furnace was discovered. This led us to modify the furnace, adding a copper insert to homogenize the temperature distribution. This late discovery casts some uncertainty on the data previously acquired.

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(1) ALL PIECES TREATED
30 min AT 600°C
NH$_3$ - PLASMA

(2) 15 min LOCALIZED
LASER IRRADIATION

(3) 30 min AT 600°C
NH$_3$ - PLASMA

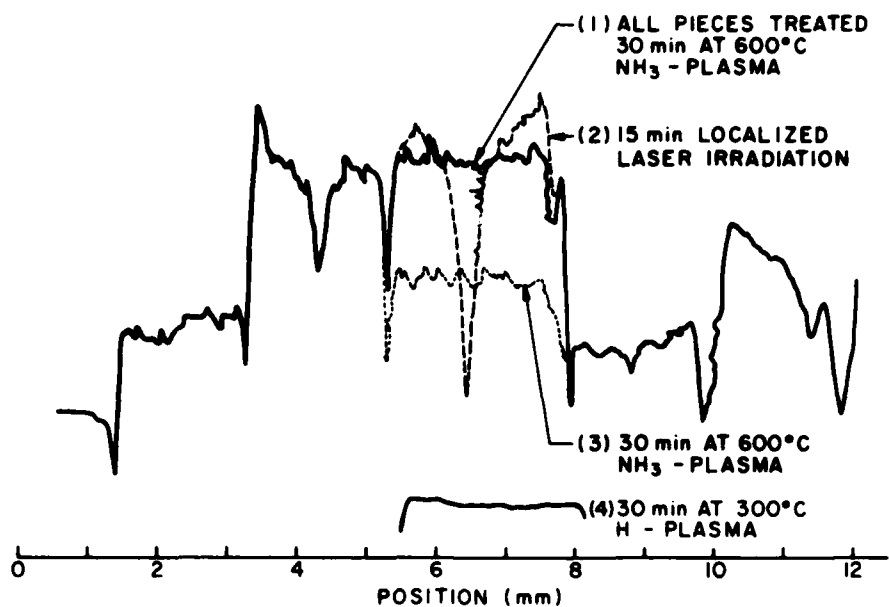(4) 30 min AT 300°C
H - PLASMA

POSITION (mm)

Figure 13.   Luminescence intensity profile of the same pieces as
in Fig. 12, but after additional treatment at 600°C
for 30 min near ammonia plasma. Then position 6.5 mm
was irradiated for 15 min at room temperature. Next,
the irradiated piece was annealed at 600°C for 30 min
with NH$_3$ plasma, and finally it was annealed at 300°C
for 30 min in atomic hydrogen.

D.   SECONDARY ION MASS SPECTROMETRY (SIMS)

Several samples were analyzed by SIMS [9] to determine the profiles of
the dominant impurities and also the arsenic concentration profile. They all
contained large concentrations of oxygen and carbon; the absolute value of the
impurity concentrations is not known at this writing, but will be determined
separately by Auger spectroscopy in the near future. Figure 14 shows SIMS-
determined profiles in a sample exposed to a nitrogen plasma. Note the de-
pletion of As at the surface where nitrogen and hydrogen seem to maximize (as
per expectation). The origin of oxygen and of carbon are still speculative.
The carbon may come from the plasma decomposition of vapors from pump oil.
Oxygen and hydrogen may come from water vapor sputtered from the walls by the
N$_2$ plasma. Oxygen may also come from the walls due to the leaching action of
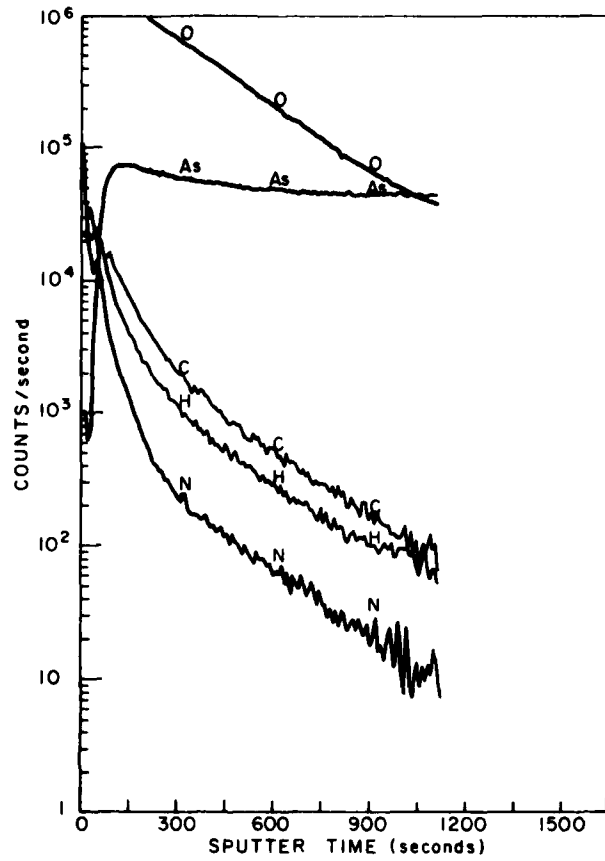gallium in the plasma.

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Figure 14.   SIMS profiles of (O), (As), (C), (H), and (N) in arbitrary units (the counts/s were not calibrated against a known concentration).

SECTION IV

CONCLUSION

The nitridization of the GaAs surface appears promising but requires further study. The improvement in surface recombination (i.e., its decrease) requires the optimization of both time and temperature of treatment. The origin and the role of impurities such as oxygen and carbon are uncertain. In the luminescence study one must also bear in mind that light-induced defects can mask the benefits of the intended surface treatment. Although the light-induced defects need to be taken into account in assaying the treatment, they may not be a problem in those practical applications where the device is sealed in an opaque encapsulation.

SECTION V

RECOMMENDATIONS FOR FUTURE STUDIES

1. The NH_3 and N_2 plasma treatments must be repeated with new precautions such as an appropriate tube liner to reduce oxygen contamination, and a cold trap to intercept the oil vapor.

2. Nitrogen should be introduced into GaAs by implantation and followed by laser annealing.

3. Also, gallium implantation followed by laser annealing may compensate for the hypothesized Ga-vacancies.

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