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Citation: J. Vac. Sci. Technol. B **23**, 1324 (2005); doi: 10.1116/1.1914820

View online: http://dx.doi.org/10.1116/1.1914820

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Protecting wafer surface during plasma ignition using an arsenic cap

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(Received 27 October 2004; accepted 21 March 2005; published 13 June 2005)

Dilute nitrides such as GaInNAs are often grown by plasma-assisted molecular-beam epitaxy (MBE), and the plasma that provides reactive nitrogen also damages the semiconductor surface. Direct exposure to the plasma has been studied extensively, but here we report damage due to indirect exposure, while the shutter remains closed. The use of a protective arsenic cap on the wafer is found to prevent such indirect damage, resulting in a 2–3*x* increase in photoluminescence intensity, sharper features in transmission electron microscopy, and a 30% decrease in laser thresholds. This technique requires no changes to the MBE chamber, unlike a gate valve. © *2005 American Vacuum Society.* [DOI: 10.1116/1.1914820]

I. INTRODUCTION

The development of dilute nitrides such as GaInNAs has opened many opportunities for lasers and detectors in the near infrared.[1] This has enabled inexpensive, monolithic vertical cavity surface-emitting lasers (VCSELs) at technologically important wavelengths near 1.3 μm.[2,3] However, the push to even longer wavelengths has been hampered by the difficulty in growing high quality material with higher amounts of nitrogen. Extensive theoretical and experimental studies have been performed on the nature of the defects in dilute nitride materials, but the microscopic causes of these defects remain uncertain.[4–6] The best results reported to date have been grown by molecular-beam epitaxy (MBE), using a nitrogen plasma cell to create reactive forms of nitrogen such as atoms, radicals, and ions. However, exposure to the plasma causes damage to the semiconductor surface during growth. Sharp reductions in defect density at high nitrogen compositions, with corresponding improvement in laser threshold current, have been achieved through the use of a small aperture to increase the pressure in the plasma cell[7–9] and the introduction of antimony.[10,11] We recently reported another sharp reduction in defects after the identification and removal of even small fluxes of ions from the plasma beam.[12] Even so, the threshold current density of GaInNAs lasers at 1.3–1.5 μm has remained higher than for equivalent InP-based lasers.

The preceding reports have focused on plasma-induced damage during the quantum well (QW) and/or GaNAs barrier growth, when the wafer is directly exposed to the plasma. However, defects before and after the QW are often overlooked as significant sources of nonradiative recombination and wafer damage. Point defects such as vacancies, even when they originate far from the QW boundary, can promote intermixing of either Group III or Group V elements, depending on whether the dominant vacancy is V_{Ga} or V_{As}.[13,14] Defects also reduce the lifetime of semiconductor lasers. They can lead to a quenching of luminescence during anneal, despite some distance from the quantum well. Finally, extended defects that were nucleated before the QW could propagate through it during growth, leading to nonradiative recombination and increased laser thresholds.

Indeed, we find that plasma-related damage of the wafer is not limited to the QWs. Deep level transient spectroscopy (DLTS) showed a high concentration of traps at the point at which the plasma was ignited, even though the nitrogen shutter was closed.[15] A Langmuir probe measurement similarly shows a strong, temporary increase in ion flux when the plasma begins to operate in high intensity (inductively coupled) mode, as shown in Fig. 1. Secondary-ion mass spectroscopy (SIMS) shows a sharp but short-lived spike in the nitrogen composition of the wafer when the plasma is ignited, as shown in two samples in Fig. 2, grown two years apart. Preventing this damage is vital to high quality GaInNAs growth.

II. ARSENIC CAPPING

One possible explanation for the additional defects at plasma ignition may be the operating point of the cell: low gas flow and high rf power may be necessary to ignite an inductively coupled (high intensity) plasma, but these conditions maximize ion production. Ions are known to cause significant wafer damage.[9,16] Several techniques have been used to minimize damage due to plasma ignition, such as burying the damaged layer under a thick GaAs buffer,[15] increased arsenic overpressure,[17] and a gate valve.[18] Wang *et al.* suggest that a growth pause with high arsenic overpressure during plasma ignition prevents excess nitridation of the surface,[17] although this disagrees with several reports that N incorporation is independent of As[19,20] above a certain As/N ratio, and a long growth pause increases the likelihood of background contaminants being incorporated in the subsequent quantum well.

Another problem with plasma sources, in addition to the generation of defects, is repeatability. Careful observation of plasma cells from several vendors has shown 5–20 min of instability before the plasma cell reaches a fully stable state.[21,22] This is believed to be due to thermal processes within the cells, at least when operating in the low-flow regime for dilute nitrides. The instability necessitates running the plasma for several minutes before the first nitride layer,

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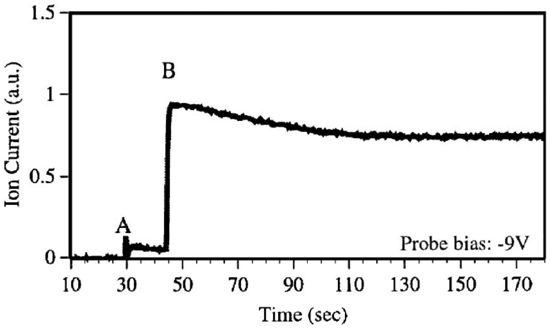

FIG. 1. Ion flux at wafer position, showing a brief transient when the plasma is first ignited in capacitively coupled mode (A) followed by a long transient to the inductively coupled mode (B).

to assure repeatable operation from run to run. In addition, the DLTS and SIMS features in Fig. 2 are not always present, suggesting they may be the result of some unknown variation in the way the plasma is ignited, despite efforts to standardize the plasma ignition process. If the plasma has not reached its stable operating point before the growth of quantum wells, there may be significant differences among the quantum wells, even emission at different wavelengths. It would be of some benefit to be able to ignite the plasma cell and adjust it to a desired state before exposing the wafer to the plasma.

Fischer *et al.* proposed the use of a gate valve between the plasma cell and the chamber, which allowed the plasma to be ignited and adjusted to a desired steady state without affecting the wafer.[18] However, the operation of a gate valve in close proximity to the nitrogen plasma can cause the plasma to become unstable again or even go out.[22] This may be evidence of an inductively coupled, parasitic load on the rf coil, as we have previously observed with a standard, tantalum MBE shutter in front of the cell. It might also be due to a change in background pressure at the exit of the plasma cell when the valve opens.

We propose the use of an arsenic cap[23] to protect the wafer during the ignition and stabilization of the plasma. This technique requires no changes to the MBE chamber and does not lead to plasma instability.

III. EXPERIMENTAL PROCEDURES

For this study, a 7 nm $Ga_{0.62}In_{0.38}N_{0.023}As_{0.95}Sb_{0.027}$ quantum well in 20 nm $GaN_{0.03}As_{0.97}$ barriers was grown using a Varian Mod-Gen II solid source MBE machine, with an SVTA model 4.5 rf plasma source to supply reactive nitrogen. The QW and growth conditions were the same as previously reported devices,[24] with 300 W of rf power, an N_2 gas flow of 0.5 sccm, and an Sb beam equivalent pressure of 1.1×10^{-7} Torr. As_2 flux was provided by a valved cracker at 15 times the Group III flux for GaAs and GaNAs growth, and 20 times for GaInNAsSb growth. All growth temperatures reported below are by uncorrected thermocouple.

Growth began with a 300 nm GaAs buffer layer. The wafer was then cooled to 10 °C for 1 h with an As flux of $0.5-1.0\times10^{-5}$ Torr in order to deposit a thick arsenic cap. To best simulate our laser growth process, the buffer growth and QW growth took place in separate MBE chambers, and the wafer was transferred under UHV while still capped. In the second chamber, the wafer was heated slowly to 160 °C, and the plasma was then ignited and operated for 20 min. A purely diffuse pattern in reflection high-energy electron diffraction (RHEED) verified that the cap remained thick and amorphous. A large arsenic flux was necessary to prevent early desorption of the cap, particularly at higher temperatures. The wafer was then rapidly heated to oxide desorption temperature (720 °C by thermocouple). The RHEED pattern showed metallic rings between 350–450 °C, then a clear 2×4 reconstruction as the last monolayers of the cap desorbed.

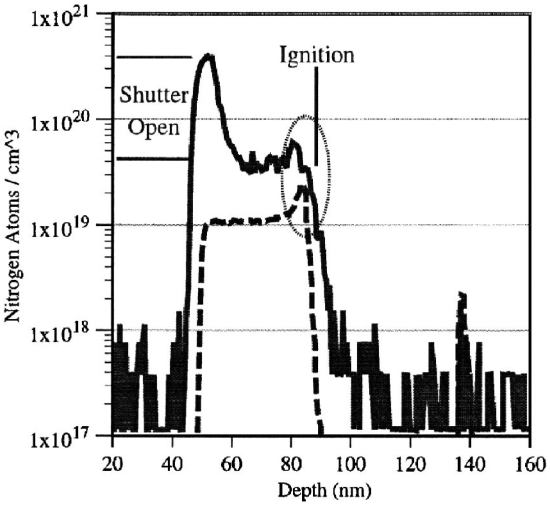

FIG. 2. SIMS depth profiles of two different samples show excess N incorporation when the plasma was ignited. The N shutter was opened only for one of the samples (solid line). The horizontal offset is not relevant to this study.

For a control, a second sample ("uncapped") was grown and capped as above, except that the arsenic cap was removed before the plasma was ignited. The wafer was heated to oxide desorption temperature, and 50 nm of GaAs was grown while progressively cooling the wafer for GaInNAs growth. The plasma was ignited as soon as soon as GaAs growth began, after the cap was completely removed. The thick GaAs had previously been believed to bury plasma-related damage, as previously mentioned.[15]

IV. RESULTS

The wafers were cleaved, and each piece underwent a rapid thermal anneal for 60 s. The room temperature photoluminescence (PL) intensities for each sample are shown in Fig. 3. The intensity was increased by 2–3 times over all annealing conditions, indicating the removal of nonradiative recombination sites. This was brighter PL than our best 1.5 μm material at the time; this was not an increase over a single, bad growth. Curiously, unlike the use of deflection plates,[12] arsenic capping does not change the annealing characteristics of the material: the luminescence begins to fall at

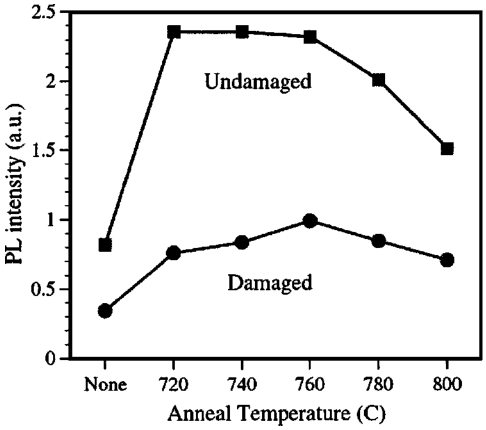

FIG. 3. 15 °C PL intensity at several anneal temperatures, for samples grown with (squares) and without (circles) extended exposure to the plasma after plasma ignition.

annealing temperatures above 760 °C. This suggests that the arsenic capping prevents a different type of damage than ion deflection plates do. The origin of the damage is unclear, but there may be high-energy neutral species leaking around the shutter, contaminants desorbed from the cryoshroud or pumps, or simply excess nitridation of the surface. The background pressures of O_2, H_2O, and CO are below 10^{-12} Torr, so that these are believed to be negligible.

Transmission electron microscopy (TEM) shows a decrease in damage with capping, and the effect on the wafer is highly localized at the cap interface. Two typical TEM (002) dark-field samples are shown in Fig. 4. These are different samples from the previously mentioned PL samples, but are typical for arsenic capped and uncapped interfaces. The reason for the change in contrast, from white to dark, is still unclear, but appears to be due to an excess of nitrogen at the capped surface, similar to the GaNAs layer visible just before the QW. The change in brightness in the QW is due to the different compositions used and is not significant for this study. For the capped sample, there does appear to be somewhat better uniformity in and between the QWs, however. We suspect that the ignition damage promotes extended defects or that nitrogen prevents their burial under subsequent growth, and this contributes to surface roughening.

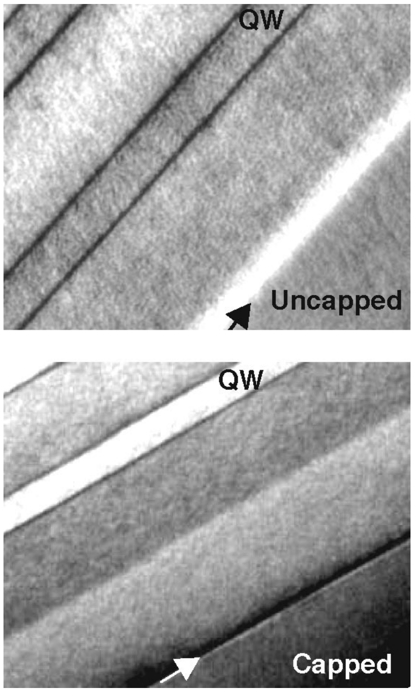

FIG. 4. Transmission electron micrograph of GaInNAsSb QW. Arrows mark the point of plasma ignition. Growth direction is toward the upper left.

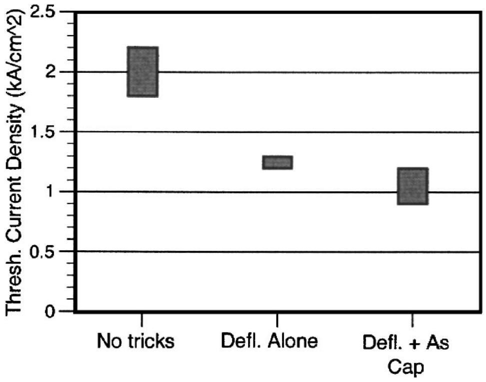

FIG. 5. Ranges of threshold current densities for edge-emitting lasers grown with ion deflection plates (middle), deflection plates, and arsenic capping (right), or neither (left).

Finally, we wished to study whether arsenic capping served the same purpose as ion deflection plates, since ion deflection could increase PL intensity by 5x.[12] Several lasers were grown without either technique, with arsenic capping alone, and with both capping and ion deflection. As Fig. 5 shows, each technique has a clear and distinct effect, so that arsenic capping is desirable even when ion deflection plates are in use.

V. SUMMARY

Defects that originate outside of the QW are commonly overlooked as sources of nonradiative recombination in GaInNAs-based lasers. The existence of such damage has been verified by SIMS, TEM, and DLTS at the layer at which the plasma was ignited in the inductively coupled (high intensity) mode. Plasma seasoning and stability would both suggest the need to allow the plasma to run for some period of time before exposing the wafer, but such exposure leads to surface damage.

This surface damage can be prevented by depositing a thick, temporary cap of solid arsenic onto the wafer surface. With the surface protected, the plasma can be ignited and tuned as desired, and the wafer is then quickly heated to growth temperatures, rapidly evaporating the excess arsenic. Unlike a gate valve, the plasma is unaffected by the start of growth. The contaminants usually associated with an extended growth interruption are avoided, although it is vitally important that growth begin as soon as possible after the cap is removed, in order to minimize damage to the exposed surface. In principle, the low-temperature GaAs layer could be reduced or eliminated as well. Using the arsenic capping technique, TEM showed better uniformity, and laser thresholds were reduced by 30%. This was shown to be independent from the use of ion deflection plates. This technique allowed the first GaAs-based VCSELs at 1.46 μm,[24] as well as the first cw, room temperature GaInNAsSb lasers beyond 1.5 μm.[25]

ACKNOWLEDGMENTS

The authors would like to thank Professor Mark Cappelli of Stanford University for helpful discussions, and Charles Evans Associates for SIMS and NRA-RBS assistance. This work was supported under DARPA and ARO contracts MDA972-00-1-024, DAAD17-02-C-0101, and DAAD199-02-1-0184, ONR contract N00014-01-1-00100, as well as the Stanford Network Research Center (SNRC) and a graduate fellowship from the National Science Foundation.

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