Nearly ideal InP/$In_{0.53}Ga_{0.47}As$ heterojunction regrowth on chemically prepared $In_{0.53}Ga_{0.47}As$ surfaces

E. Yablonovitch, R. Bhat, C. E. Zah, T. J. Gmitter, and M. A. Koza
Bell Communications Research, Navesink Research Center, Red Bank, New Jersey 07701-7040

(Received 30 September 1991; accepted for publication 14 November 1991)

When III-V growth is interrupted for processing, in the ambient laboratory environment for example, regrown heterojunction quality has been rather disappointing in comparison to uninterrupted epitaxial growth. We have conducted a search for surface chemical preparations on $In_{0.53}Ga_{0.47}As$ which would produce the highest-quality InP/$In_{0.53}Ga_{0.47}As$ regrown heterojunction interface, as measured by surface recombination velocity (SRV). After an extensive survey, we have found that dilute bromine-based etching solutions are best for preparing a free $In_{0.53}Ga_{0.47}As$ surface for subsequent InP regrowth. The resulting InP/$In_{0.53}Ga_{0.47}As$ interfacial SRV is $\lesssim 20$ cm/s, comparable to heterojunctions grown without any interruption at all.

Ideal heterojunctions, a necessity for III-V optoelectronics, have generally been produced by uninterrupted epitaxial growth. As we have moved toward smaller devices, where exposed edges and surfaces play a greater role, optoelectronics has needed some type of edge heterojunction or surface passivation. Two approaches have been used: (1) simple regrowth of a III-V heterojunction on the exposed surface, (2) a permanent chemical coating.

If there is no special surface chemical preparation, the regrown III-V heterojunctions are generally no better than the original bare surface. In the case of GaAs it was discovered[1] that sulfide chemistry can be very beneficial for surface electronic quality. For purposes of AlGaAs regrowth, $(NH_4)_2S$ solutions[2,3] or selenide solutions[4] are particularly effective at preparing GaAs surfaces for the growth chamber. A permanent coating of As_2S_3 glass[5] on GaAs produces a similar improvement in surface recombination velocity (SRV). Nevertheless, neither AlGaAs regrowth nor As_2S_3 glass coating on GaAs has a SRV any lower than $\sim 10^4$ cm/s.

For perspective, it is important to realize that the different III-V semiconductors have very different surface quality. Without question, GaAs has one of the worst free surfaces in solid-state electronics. A survey[6] of surface recombination velocities for various semiconductors is shown in Fig. 1. SRV is a type of inverse figure of merit. For ordinary oxidized GaAs surfaces, SRV $\gtrsim 10^6$ cm/s. This is to be contrasted with oxidized $In_{0.53}Ga_{0.47}As$ alloy surfaces which start out around 5000 cm/s. Apparently the indium alloy content[7] makes the surface properties very forgiving. Therefore it is sensible to employ InGaAs alloys in any optoelectronic application where edge or surface passivation will be a major variable. Indeed, naked $In_{0.53}Ga_{0.47}As$ quantum wells[8] can have good photoluminescence and a controllable quantum shift.

In our experiments we have surveyed surface chemical preparations on $In_{0.53}Ga_{0.47}As$ which would produce the highest-quality InP/$In_{0.53}Ga_{0.47}As$ regrown heterojunction interface, as measured by surface recombination velocity. After an extensive survey, we have found that bromine-based etching solutions, HBr:(Br sat. H_2O):H_2O (1:1:10), or Br:CH_3OH (1:2000) are best for preparing a free $In_{0.53}Ga_{0.47}As$ surface for subsequent InP regrowth. The resulting InP/$In_{0.53}Ga_{0.47}As$ interfacial SRV is $\lesssim 20$ cm/s, comparable to heterojunctions grown without any interruption at all. There have also been recent studies[9] of surface chemical preparation of InP for regrowth of the inverted heterojunction $In_{0.53}Ga_{0.47}As$/InP, with good results.

Our survey was conducted by means of a contactless laser-pumped carrier lifetime bridge[6] as shown in Fig. 2. An inductively coupled radio-frequency apparatus moni-

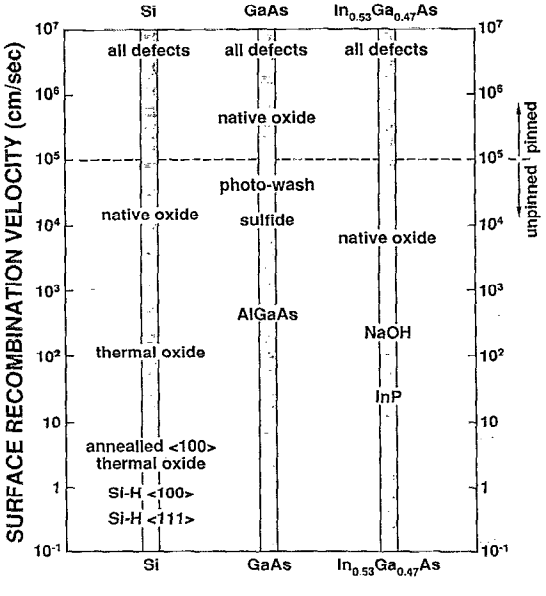

FIG. 1. Summary of many different chemically prepared semiconductor surfaces, covering a dynamic range of eight decades in surface recombination velocity (SRV). InP and AlGaAs are of course lattice-matched heterostructures. The Si-H surface is measured under acid. "All defects" refers to the worst possible case of virtually every surface bond being defective, which may apply to oxidized GaAs surfaces. Pinned and unpinned is only a qualitative distinction, which occurs around SRV $\sim 10^5$ cm/s. Plainly, the $In_{0.53}Ga_{0.47}As$ surfaces and interfaces are very forgiving. Native oxide covered $In_{0.53}Ga_{0.47}As$ starts with a lower SRV than sulfide-treated GaAs.

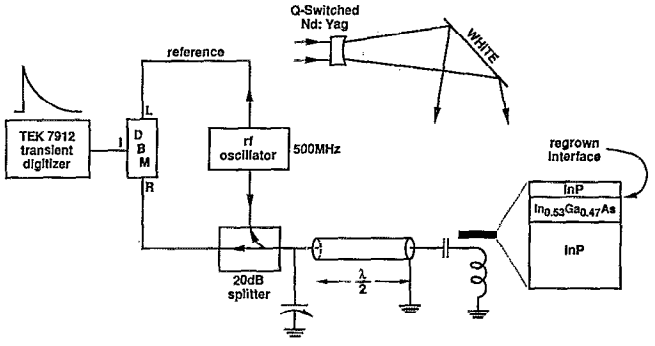

FIG. 2. Infrared Nd:YAG laser scatters off a white surface and injects carriers into a $InP/In_{0.53}Ga_{0.47}As/InP$ double-heterostructure epilayer. The transient conductivity is probed by rf induction at 500 MHz. The series resonant circuit, adapted from NMR technology, includes a $\lambda/2$ section of co-ax for convenient access to the tuning element. A 20 dB splitter separates the incoming from the reflected signal. The imbalance in the circuit caused by the carriers is phase detected by a wide dynamic range double-balanced mixer (DBM), and then digitized.

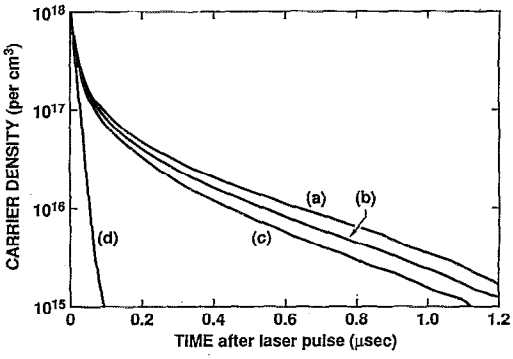

FIG. 3. (a) Carrier-density decay in an optically excited $InP/In_{0.53}Ga_{0.47}As/InP$ double heterostructure made by uninterrupted growth. (b) Growth interrupted by etching the $In_{0.53}Ga_{0.47}As$ in HBr:(Br sat. H_2O):H_2O, (1:1:10). The minority-carrier lifetime deteriorates only slightly. (c) Growth interrupted by etching the $In_{0.53}Ga_{0.47}As$ surface in H_2SO_4:H_2O_2:H_2O (1:8:5000). (d) A chemical oxide covered $In_{0.53}Ga_{0.47}As$ top surface, no InP regrowth.

tors the absolute sheet conductivity of the semiconductor as a function of time. A short pulse of incoherent light from a Q-switched Nd-YAG laser injects electrons and holes into an $InP/In_{0.53}Ga_{0.47}As/InP$ double-heterostructure epilayer grown by organometallic chemical vapor deposition (OMCVD). The recombination of electrons with holes is monitored by the decay of the conductivity associated with the optically injected carriers. If the epilayer thickness L is sufficiently small, the decay of excess carrier density n is simply the sum of a bulk and a surface term[10]:

$$\frac{dn}{dt} = -\left(\frac{1}{\tau_b} + \frac{S_f + S_r}{L}\right)n, \tag{1}$$

where τ_b is the bulk recombination lifetime, S_f is the SRV of the front heterojunction which is accessible for regrowth, and S_r is the SRV of the rear $In_{0.53}Ga_{0.47}As/InP$ heterostructure interface which remains intact throughout the experiments. The reciprocal of the quantity in brackets in Eq. (1) was called by Shockley[11] the "filament lifetime" τ, which in general may depend on n. Irrespective of the absorption depth of the light source, the injected carrier density n will become spatially uniform and Eq. (1) will be valid provided that $L \ll \sqrt{D\tau}$, where D is the ambipolar diffusion constant and $\sqrt{D\tau}$ is the diffusion length. This was easily satisfied in these experiments since the $In_{0.53}Ga_{0.47}As$ epilayer thickness was $L = 0.5$ μm.

Our starting point is the measured density decay curve in Fig. 3(a) of an intact undoped $InP/In_{0.53}Ga_{0.47}As/InP$ double-heterostructure (DH) epilayer as made by uninterrupted growth. Then the upper InP layer is selectively etched away, using HCl acid, exposing a free $In_{0.53}Ga_{0.47}As$ surface. Following surface chemical treatment and InP regrowth on the bare $In_{0.53}Ga_{0.47}As$, the density decay was measured again on the same sample. The density decay curves for the original intact DH and the same DH subjected to interrupted regrowth are shown in Fig. 3. The initial nonexponential character of the DH decay curve is due to the influences of bulk Auger and radiative recombination.

By employing the original uninterrupted-growth DH decay curve, in Fig. 3(a), as a reference we can subtract the effect of bulk recombination, leaving only the difference in SRV between the interrupted and uninterrupted growth $InP/In_{0.53}Ga_{0.47}As$ top heterojunction as the measured quantity. Specifically, the logarithmic derivative $(1/n)(dn/dt)$ of the density decay curve is the reciprocal filament lifetime $1/\tau$. At a given density, the difference in reciprocal filament lifetime between the interrupted and uninterrupted-grown $InP/In_{0.53}Ga_{0.47}As$ heterojunction is $(S_f^i - S_f)/L$. Therefore all the measurements in this letter are with respect to S_f, the original uninterrupted-growth SRV. For $InP/In_{0.53}Ga_{0.47}As$, S_f is so slow, $\lesssim 20$ cm/s, as to be very difficult to measure. (The SRVs quoted in this letter are all reported at 10^{16} cm^{-3} injection level.)

Our surface chemical treatments always began with HCl acid selective etching which stops at the top surface of the $In_{0.53}Ga_{0.47}As$. Apparently the exposed heterojunction interface has some unusually favorable chemical stability. If the sample is reinserted into the growth chamber shortly after etching off the InP, the regrown $InP/In_{0.53}Ga_{0.47}As$ carrier-density decay curve is indistinguishable from the original curve 3(a)! Such excellent behavior occurred on every fresh sample which we tested. While this is an outstanding result, it is not particularly useful, since the $In_{0.53}Ga_{0.47}As$ itself was not actually etched or processed. In order to simulate useful processing conditions, such as etch patterning of the $In_{0.53}Ga_{0.47}As$, we tested a number of different surface etching and preparation protocols.

Curve 3(b) shows the results of regrowth after one of our best etching protocols. The chemical surface treatment consisted of the following: step (1), selective removal of the InP using HCl acid; step (2), etching the $In_{0.53}Ga_{0.47}As$ for 5 s in {HBr:(Br saturated H_2O):H_2O, 1:1:10}, removing about 4 nm of material. Following a sometimes protracted waiting period, for the availability of the OMCVD growth chamber, there came step (3), a

TABLE I. The surface recombination velocity on regrown InP/$In_{0.53}Ga_{0.47}As$ heterojunctions (in cm/s, referenced to an uninterrupted-growth heterojunction) for various surface preparations on the $In_{0.53}Ga_{0.47}As$.

Chemical preparation method	$(S_f^i - S_f)$
HCl acid only [no step (2)]	$\lesssim$20 cm/s
HBr:(Br sat. H_2O):H_2O, 1:1:10	$\lesssim$20 cm/s
Br:CH_3OH, 1:2000	$\lesssim$20 cm/s
H_2SO_4:H_2O_2:H_2O, 1:8:5000	$\sim$50 cm/s
H_2SO_4:H_2O_2:H_2O, 1:8:500	$\sim$100 cm/s
H_2SO_4:H_2O_2:H_2O, 1:8:500 followed by $(NH_4)_2S$ rinse	$\sim$200 cm/s
H_2SO_4:H_2O_2:H_2O, 1:8:500 followed by $(NH_4)_2S$ rinse delete conc. H_2SO_4 shortly before regrowth	$\sim$200 cm/s
No InP regrowth after oxidizing etch	$\sim$5000 cm/s

cleaning rinse in concentrated H_2SO_4 for 2 min shortly before regrowth. Each of the above steps was followed by a de-ionized water rinse. The measured $(S_f^i - S_f)$ in curve 3(b) was $\lesssim$20 cm/s, comparable with the uncertainty in S_f.

Curve 3(c) shows another good regrowth treatment. The sample was subject to the same series of chemical steps as in 3(b) except that the etching in step (2) was changed. In 3(c) the step (2) etchant was H_2SO_4:H_2O_2:H_2O (1:8:5000) for 30 s which removes about 6 nm of $In_{0.53}Ga_{0.47}As$. The measured $(S_f^i - S_f)$ in curve 3(c) was $\sim$50 cm/s, also a good result. Curve (d) shows the carrier-density decay from a sample which experienced steps (1) and (2), making a chemical oxide on the $In_{0.53}Ga_{0.47}As$, but no InP regrowth.

A summary of most of our other chemical etching treatments appears in Table I. Among the most noteworthy is {Br:CH_3OH, 1:2000} for which $(S_f^i - S_f) \lesssim 20$ cm/s. Clearly the two bromine-based etchants seem to give the best regrowth results. In some situations the water-based etchant is advantageous[12] since it does not attack photoresist. The H_2SO_4:H_2O_2:H_2O etchants are not as good, but they perform better if they are more dilute. $(NH_4)_2S$ is not an etchant, but its beneficial effects on oxidized GaAs are well known.[1] On $In_{0.53}Ga_{0.47}As$, however, it has previously been observed[8] that oxide chemistry is more effective than sulfide chemistry for the surface properties. This is once again confirmed in Table I. $(NH_4)_2S$ does not improve regrowth quality of the oxidized $In_{0.53}Ga_{0.47}As$ surface formed by H_2SO_4:H_2O_2:H_2O etchants.

Let us now discuss the implications of InP/$In_{0.53}Ga_{0.47}As$ regrowth for the formation of narrow buried heterostructures and laterally quantized device structures. HBr:(Br sat. H_2O):H_2O has already shown[13] its usefulness for patterning buried-heterostructure lasers before regrowth. Very fine lines can be patterned into $In_{0.53}Ga_{0.47}As$, both by wet or dry etching. These bromine-based etches can be used to remove any radiation damaged or ion-beam damaged surface regions. At the same time they prepare the surface for regrowth of a buried structure. If the lateral dimension of the buried $In_{0.53}Ga_{0.47}As$ structure is as narrow as $\sim$10 nm, it implies a minority-carrier lifetime $\sim$10 ns. This permits the formation of light-emitting structures which are not interface defect limited, but limited only by intrinsic properties of the material.

We would like to thank Dave Aspnes for suggesting the Br:CH_3OH etch.

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