

Nearly ideal electronic surfaces on naked $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ quantum wells

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We have discovered that hydroxide-coated $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ has the lowest known surface recombination velocity of any III-V semiconductor. To demonstrate the excellent electronic quality of such interfaces, we have measured the quantum shifts in the room-temperature luminescence spectrum of "naked" $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ quantum wells (i.e., quantum wells with one face uncovered) in the thickness range 15–50 Å. These nearly ideal electronic surfaces should allow the fabrication of lateral quantum confinement structures that operate at room temperature.

The use of chemical methods to create nearly ideal electronic surfaces on semiconductors has recently become tremendously successful. The lowest known surface recombination velocity (SRV) for any semiconductor surface or interface, 0.25 cm/s, occurs on chemically¹ prepared Si(111). Interest in passivating GaAs surfaces has been even more intense.^{2–6} In a broad survey of various chemical treatments for the III-V semiconductors, using contactless photoconductivity decay, we discovered⁷ that $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ produced a GaAs surface whose electronic quality approached that of the AlGaAs/GaAs interface. This improvement in surface electronic quality led to a 60-fold increase in the gain of GaAs heterojunction bipolar transistor.⁸

We have now extended our survey to $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, a very important semiconductor in the field of photonics. The indium-based semiconductors seem to share the property of having fairly reasonable⁹ surface electronic quality even without special chemical treatment. Under a native oxide, we find¹⁰ that the SRV of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ at room temperature is only ~ 5000 cm/s. Moreover, at liquid-helium temperatures, surface recombination processes appear to be completely frozen out,^{11,12} permitting efficient luminescence. Any further improvement in the quality of the $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ surface would make it comparable to the best lattice-matched heterostructures such as $\text{InP}/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$. We have discovered that a hydroxide (NaOH, KOH, etc.) chemical coating results in the lowest SRV of any of the reagents that we have tested so far. The SRV of ~ 200 cm/s on hydroxide-coated $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ is the lowest ever reported on any III-V semiconductor non-epitaxial interface, including sulfide-coated GaAs.⁷

To demonstrate the excellent electronic quality of such chemically passivated surfaces, we have constructed "naked" quantum wells (i.e., quantum wells in which one face has been uncovered) and have measured the quantum shifts in the photoluminescence spectra. Accessibility of one face of the quantum well permitted us to gradually etch the well thickness from ~ 50 to ~ 15 Å, monitoring the quantum shift along the way.

The SRV was measured with a contactless laser-pumped carrier lifetime bridge.⁷ An inductively coupled radio frequency apparatus monitors 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 $\text{InP}/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$

double-heterostructure epilayer. 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 term⁷:

$$\frac{dn}{dt} = -\left(\frac{1}{\tau_b} + \frac{S + S_h}{L}\right)n, \quad (1)$$

where τ_b is the bulk recombination lifetime, S is the SRV of the front surface, which is accessible for chemical modification, and S_h is the SRV of the rear $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$ heterostructure interface. The reciprocal of the quantity in brackets in Eq. (1) was called by Shockley¹³ 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.

Our starting point was the measured density decay curve of an intact undoped 0.65- μm -thick $\text{InP}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$ double-heterostructure epilayer, as shown in Fig. 1(a). Then the upper InP layer was selectively etched away, exposing a free $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ surface. Following interfacial chemical treatment, the density decay was measured again on the same sample. The density decay curves for the original intact double heterostructure and a number of chemical preparations are shown in Fig. 1. The initial nonexponential character of the double-heterostructure decay curve is due to the influences of bulk Auger and radiative recombination. By employing the double-heterostructure decay curve as a reference, we can subtract the effect of bulk recombination, leaving only the difference in SRV between the $\text{InP}/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ interface and the chemically modified surface 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 chemically prepared surface and the reference $\text{InP}/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ interface is $(S - S_h)/L$.

Likewise, we can thin the sample chemically and plot the reciprocal filament lifetime versus reciprocal thickness L , as is frequently done² in studies of SRV. As seen from Eq. (1), the slope of the resulting line is simply $S + S_h$. Combin-

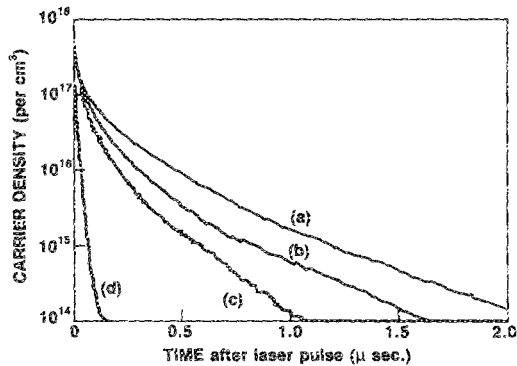


FIG. 1. Decay of carrier density in an InP/In_{0.53}Ga_{0.47}As/InP double heterostructure excited by delta function optical injection at $t = 0$. (a) The intact InP/In_{0.53}Ga_{0.47}As/InP double heterostructure. (b) Aqueous 10 M NaOH/In_{0.53}Ga_{0.47}As after 30 min at $T = 20^\circ\text{C}$. (c) Spun-dry NaOH/In_{0.53}Ga_{0.47}As after a 30 min soak. (d) Native oxide/In_{0.53}Ga_{0.47}As.

ing the sum and difference expressions, we can then determine S and S_h separately.

Returning now to Fig. 1, we can compare the decay curves resulting from a number of different surface preparations with that of the InP/In_{0.53}Ga_{0.47}As heterostructure. The highest curve, (a), is for the intact double heterostructure. Curve (b) is for an In_{0.53}Ga_{0.47}As surface that has experienced the following two-step preparation procedure: Step (1): The surface is etch cleaned in H₂SO₄:H₂O₂:H₂O (1:8:5000). Step (2): The sample is then immersed in 10 M NaOH solution at $T = 20^\circ\text{C}$. The decay curve, monitored *in situ* in solution, gradually improves over a 30 min period to that shown as (b). The difference between (a) and (b) represents $S - S_h$, as discussed. When the sample is then spun dry in air, leaving behind a thin polycrystalline NaOH film, curve (c) results. The dry film SRV is somewhat higher than that in solution. Finally, curve (d) represents the comparatively poor performance of a native-oxide-coated In_{0.53}Ga_{0.47}As sample that has an SRV of ~ 5000 cm/s.

A careful analysis of the shapes of the decay curves shows that, for case (b), at least, negligible surface charge is present to bend the bands. This should be compared to the small amount that was indeed detected⁷ for sodium-sulfide-coated GaAs. The sum and difference measurements of SRV led to $S \approx 250$ cm/s and $S_h \approx 45$ cm/s for case (b). The dry NaOH film in case (c) had $S \approx 250$ cm/s. The value for S_h resembles previous¹⁴ measurements on InGaAsP.

In order to study the effect of the NaOH coating on quantum wells, a very thin and uniform layer of In_{0.53}Ga_{0.47}As was required. The epitaxial structure, consisting of 50 Å of In_{0.53}Ga_{0.47}As on a 3000 Å InP buffer layer, was grown by chloride vapor levitation epitaxy¹⁵ in a dual growth chamber system at 550 °C. The substrate was Fe-doped semi-insulating InP oriented 3° off (100) toward the closest (110) axis. At this lower-than-usual growth temperature, a very low growth rate is possible. The 50 Å In_{0.53}Ga_{0.47}As layer required 60 s growth time, whereas the wafer was transferred from the InP growth chamber to the In_{0.53}Ga_{0.47}As growth chamber in less than one-half second. This results in extremely sharp heterointerfaces, even without interruption of growth between layers. Transmission electron microscopy confirmed approximately monolayer

abruptness for an 11 Å In_{0.53}Ga_{0.47}As/InP quantum well grown under the same conditions.¹⁶ Spectral ellipsometry and x-ray diffraction were also used to study the thin films. Band-to-band room-temperature photoluminescence was excited by a focused 0.63 μm, 5 mW He-Ne laser, of pump intensity 500 W/cm², below the threshold for nonlinear band-filling effects, which could have distorted the spectra in Fig. 2. Because of the hygroscopic character of NaOH, it was desirable to flow dry N₂ over the sample during the photoexcitation to prevent photoetching.

For reference purposes a luminescence spectrum from bulk In_{0.53}Ga_{0.47}As is shown on the right side of Fig. 2. The spectrum marked "begin" was obtained with the original as-grown ~ 50 -Å-thick epilayer. The linewidth indicates reasonable uniformity of epilayer thickness and composition, within the limited resolution available at 300 K. Then the epilayer was thinned in a very dilute etchant, H₂SO₄:H₂O₂:H₂O (1:8:50 000), which was independently measured to have an etch rate of ~ 20 Å per minute. At approximately 10 s intervals, the samples were removed from the etchant, rinsed, coated with NaOH, and a photoluminescence spectrum was recorded. The resulting series of spectra are given in Fig. 2 with the total etch time shown in seconds. There is a smooth quantum shift as a function of etch time. After 95 s of etching, the surface of the InP was almost bare, except for a few small patches that had the luminescence spectrum marked as "95 s" in Fig. 2.

The spectral shifts were modeled by solving Schrödinger's equation for electron and hole quantum wells. The In_{0.53}Ga_{0.47}As/InP heterojunction band offsets¹⁷ are among the most accurately known III-V barrier heights. Since NaOH is a wide band-gap dielectric, the surface discontinuity was taken as infinite relative to the heterojunction offsets of only 0.2 and 0.35 eV. It is interesting to note that, even at the outset before etch thinning, the electron and hole wave functions are shared between the very thin In_{0.53}Ga_{0.47}As surface layer and the InP substrate. As the In_{0.53}Ga_{0.47}As becomes thinner and thinner, the carriers have more and more of their probability amplitude in the InP, with the electrons eventually becoming unbound because of the shallowness of the electron potential well in this heterojunction. Contrary to the usual symmetrical quantum wells, which

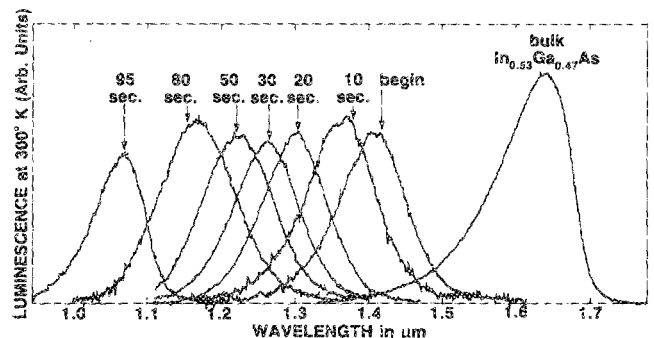


FIG. 2. Band-to-band room-temperature photoluminescence from a 50-Å-thick NaOH coated "naked" quantum well as it is gradually thinned down by slow etching. The spectrum marked "begin" is the starting point. The quantum-shifted spectra induced by etch thinning for a given number of seconds are shown. The absolute intensities are given in Fig. 3. The spectrum at 95 s is distorted because of a silicon window in the optical train.

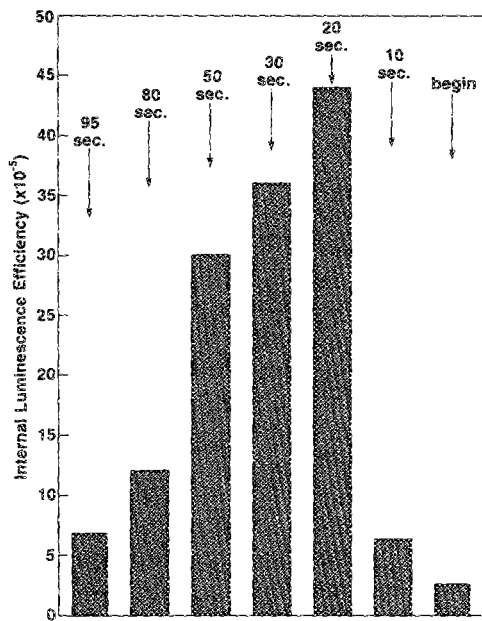


FIG. 3. Absolute luminescence efficiency referenced to a 1.52 μm He-Ne laser for the various etch times of the spectra in Fig. 2. A few monolayers of surface $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ must be removed by etch cleaning during the first 20 s in order for the full benefit of the NaOH film on the surface electronic properties to make itself felt.

always have at least one bound state, one-sided quantum wells may have no bound states if they are sufficiently shallow. In effect, a miniscule amount of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ coating on an InP wafer confines a surface 2D hole gas, which recombines radiatively with a 3D electron gas. Excitonic binding is negligible at room temperature.

There has been considerable interest¹⁸ in laterally confined quantum dot structures, but the exposed edges left behind after lithographic patterning have very poor electronic properties. Chemical means of "healing" the exposed surfaces should be very helpful in extending our ability to study structures that are small in all three dimensions. Such quantum dots on an InP surface can be pumped by electronic injection if they are within a diffusion length of a p - n junction.

The absolute luminescence efficiency was measured by referencing the photoluminescence signals to light elastically scattered from a white surface illuminated by a 1.52 μm He-Ne laser in the identical optical system. Luminescence efficiencies, corresponding to the spectra in Fig. 2, are shown in Fig. 3. As explained above, the surface preparation is a two-step process: the NaOH film is ineffective without preliminary etch cleaning. It is clear from Fig. 3 that 20 s of etch cleaning are required for the full benefit of spin coating the NaOH film. This corresponds to the removal of the top few atomic layers of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, in order to get the full 20-fold increase in luminescence.

We now discuss some variations in the chemical preparation procedure. As explained above, it consisted of an

etch-cleaning step, a 30 min soak in 10 M NaOH, followed by a spin coating. The 30 min period could be reduced to 5 min if preceded by a rinse in $(\text{NH}_4)_2\text{S}$. Furthermore, the presence of the pulsed Nd:YAG laser during the lifetime decay measurements seemed to have a slightly beneficial effect, suggesting some photochemical² action. The coated $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ surface is relatively durable, especially in a dry environment. After a few days, the SRV climbed by a factor 2, but then it remained essentially constant after four weeks of aging.

Both $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and NaOH have very beneficial effects on both GaAs⁷ and $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ surfaces. For GaAs, films of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ have the advantage, while for $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, films of NaOH are superior. The absolute differences are small compared to the big improvements over the untreated surfaces. The very low SRV's correspond to a miniscule density of defective surface bonds.

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¹⁰Unless otherwise noted, the values of S quoted in this article are for a bulk injection level $n \approx p \sim 10^{16}/\text{cm}^3$.

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