As_2S_3/GaAs, a new amorphous/crystalline heterojunction for the III-V semiconductors

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Much of the technology of our era is based on the SiO_2/Si amorphous/crystalline heterojunction interface. Now it appears that As_2S_3/GaAs amorphous/crystalline heterojunctions show some technological promise. We have found that properly prepared As_2S_3/GaAs interfaces can have reasonably good electronic quality. The interfacial recombination velocity is $\approx$15 000 cm/s at flat band, which results in a $\sim$100-fold reduction of perimeter recombination currents in *p-n* junction mesas. This can be important on heterojunction transistor emitter-base perimeters, solar cell and light-emitting diode perimeters, and for reducing mirror facet recombination in semiconductor lasers.

Much of the technology of our era is based on the SiO_2/Si amorphous/crystalline heterojunction interface. The hallmark of electronic interfacial science is the low density of electronically active defects at the surface of the semiconductor. Additionally, the amorphous layer acts as a diffusion barrier to encapsulate and protect the highly perfect interface. For III-V semiconductors there has been no similar material system available.

We have now found that properly prepared As_2S_3/GaAs amorphous/crystalline interfaces can have reasonably good electronic quality. As_2S_3 is an excellent glass,[1] very difficult to devitrify, with a band gap of $\approx$2.4 eV. It is insoluble in water and is a rather durable material which can make a permanent surface passivation on the III-V semiconductors. Some properties of As_2S_3 glass are listed in Table I. As in the case of the SiO_2/Si interface, the materials processing history of the interface is equally important as its chemical composition in reducing the electronically active defect density. In this letter we will present some processing protocols which have allowed us to create interfaces with an interfacial recombination velocity of $\approx$15 000 cm/s at flat band, about a 100-fold improvement over ordinary GaAs surfaces.

The key to our experimental approach has been the contactless laser-pumped minority-carrier lifetime probe.[2] This inductively coupled radio frequency bridge allows rapid contactless monitoring of interfacial electronic quality on partially processed wafers. Since we can measure interfacial quality within about a minute, our empirical, Edisonian approach can actually be quite efficient. We feed minority-carrier lifetime information directly back into the material preparation. Therefore we can quickly converge onto an excellent quality interface. Using this philosophy we have discovered a number of interesting electronic interfaces on Si (Ref. 3) and the III-V's.[4,5]

In these experiments, a *Q*-switched doubled Nd:YAG laser injects carriers into a 2-μm-thick $Al_{0.5}Ga_{0.5}As$/GaAs/$Al_{0.5}Ga_{0.5}As$ double heterostructure. The minority-carrier lifetime bridge reads out directly in terms of carrier density versus time after injection, as shown in Fig. 1(a). The slow exponential decay at densities below $10^{17}/cm^3$ is due to nonradiative recombination centers.[2] After the top layer of $Al_{0.5}Ga_{0.5}As$ is selectively removed in HF acid, the carrier density decay in Fig. 1(d) is much faster due to nonradiative recombination on the oxidized GaAs surface.

At this point, any one of a number of surface chemical processing sequences may be invoked in order to restore the interfacial quality. We had previously discovered[4] that a class of inorganic sulfides [Li_2S, $(NH_4)_2S$, $Na_2S\cdot9H_2O$, etc.] were quite effective for this purpose. Nevertheless, their range of applicability was severely limited since the exposed GaAs surfaces would eventually deteriorate over time. Accordingly we have sought a form of sulfide chemistry which would produce a permanent heterojunction-type interface. As_2S_3 glass seemed an excellent choice, but it was necessary to find a processing protocol that maintained the best possible interfacial quality. Table II is the result of an extensive series of experimental runs as monitored by the minority-carrier lifetime bridge.

After the usual oxidative cleaning and rinsing procedures, the coating steps are (5) and (6) in Table II. The GaAs is soaked in a 0.16 M As_2S_3 dissolved in concentrated NH_4OH, with methanol added as a wetting agent. Then the wafer is simply spun dry, leaving a film of As_2S_3, $\sim$100 nm thick. Alternatively the solution may be permitted to dry without spinning, leaving a thick layer of As_2S_3. The final three steps, (7), (8), and (9) are for the purpose

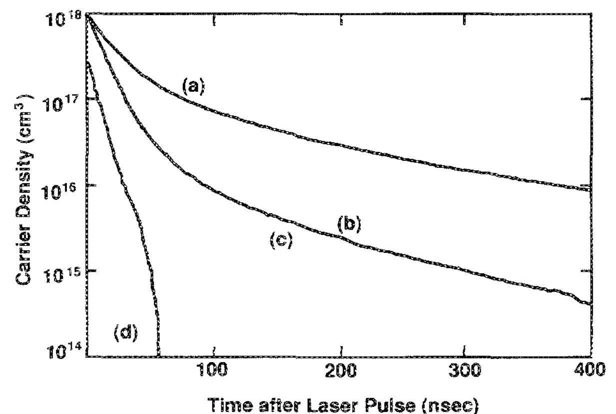

FIG. 1. Decay of carrier density in an $Al_{0.5}Ga_{0.5}As$/GaAs/$Al_{0.5}Ga_{0.5}As$ double heterostructure excited by delta function optical injection at $t = 0$. (a) The intact original double heterostructure. (b) As_2S_3/GaAs/$Al_{0.5}Ga_{0.5}As$ double heterostructure immediately after preparation by the procedure in Table II. (c) The same sample after being aged on the shelf for four months. (d) The same sample with an exposed oxidized GaAs surface.

TABLE I. Some properties of As_2S_3 glass.

Band gap	2.4 eV
Refractive index	2.6
Crystal melting point	315 °C
Glass transition temp.	~195 °C
Resistivity	10^{18} Ω cm
Soluble in	conc. NH_4OH

of annealing to form a dense, structurally interconnected network glass of As_2S_3. It is essential that the annealing tube be entirely purged of air *before* heating it. The resulting glass is relatively impermeable, so that the interface electronic quality is protected permanently. The annealing should be done with care, since the vapor pressure of As_2S_3 can be significant at temperatures of 300 °C and above.

The effect of the protocol in Table II on the carrier density decay curves of an As_2S_3-coated double heterostructure is shown in Fig. 1(b). The strong laser pulse substantially flattens the bands, reducing the effects of band bending[4,6] on the surface recombination velocity. A careful accounting of band bending effects on the curve in Fig. 1(b), similar to Ref. 4, yields a surface recombination velocity $S_0 \approx 1.5\times10^4$ cm/s at flat band.

After aging on the shelf for four months the structure was tested again, resulting in Fig. 1(c). This overlaid perfectly on Fig. 1(b), so only one curve could be shown. We have conducted accelerated aging tests, for example 15 min at 225 °C in air, with no deterioration. We believe the durability of the As_2S_3/GaAs electronic interface is limited only by diffusion through the As_2S_3 glass.

We tried other methods of making As_2S_3/GaAs. Simply evaporating As_2S_3 onto GaAs did not improve the surface electronic quality over that of an oxidized GaAs surface. This was in spite of cleaning the GaAs surface with $(NH_4)_2S$ prior to loading into the evaporator. This shows that processing history is the essential variable in establishing a worthwhile As_2S_3/GaAs interface, but it would be speculative to invoke a specific physical mechanism. A prior study[7] of lateral electrical transport in As_2S_3 thin films on semiconductors, employed simple evaporation as the preparation method.

After the original discovery[4] of the sulfide surface passivations on GaAs, the first application[8] was directed toward perimeter currents at the emitter-base junction of heterojunction bipolar transistors. Perimeter recombination currents are also known to degrade the efficiency of solar cells.[9] Furthermore, some evidence has now accumulated,[10] that mirror facet recombination currents are responsible for local heating and catastrophic optical damage[11] in semiconductor lasers. Accordingly, we have applied the As_2S_3 glass to diode mesas in order to measure the perimeter recombination currents at the edges of a *p-n* junction.

The particular mesa structure which we investigated is shown in Fig. 2. The wafer had originally been grown for making conventional double-heterostructure diode lasers. The behavior of other types of diode structures should be similar, however.

A series of circular diodes were mesa etched to have

TABLE II. An optimal processing sequence for As_2S_3/GaAs.

(1)	Oxidize GaAs surface in 1:8:500 (H_2SO_4:H_2O_2:H_2O).
(2)	De-ionized water rinse, flowing, 30 s.
(3)	Soak 5 min in $(NH_4)_2S$, 22% conc.
(4)	De-ionized water rinse, flowing, 20 s.
(5)	Soak 5 min in 0.16 M As_2S_3 dissolved in conc. NH_4OH mixed 2:1 with CH_3OH, as a wetting agent.
(6)	Spin dry at 2500 rpm.
(7)	Load into cold furnace tube under flowing forming gas, 10 min.
(8)	Place tube in furnace and anneal for 2 min at 290–300 °C under flowing gas. The vapor pressure of As_2S_3 at the annealing temperature is significant. Over-annealing will cause the As_2S_3 layer to be lost by sublimation.
(9)	Remove tube from furnace and cool quickly down to room temperature

diameters 500, 100, and 60 μm. Following Stellwag *et al.*,[12] the forward current-voltage (*I-V*) characteristic is expected to be of the following form:

$$I=I_1(e^{qV/kT}-1)+J_{nA}A(e^{qV/nkT}-1)$$
$$+J'_{nP}P(e^{qV/nkT}-1)\,, \qquad (1)$$

where I_1 is the diffusion saturation current, J_{nA} is the area-related forward recombination current density (A/cm^2), J'_{nP} is the perimeter-related recombination current density (A/cm), A is the area of the diode, and P is its perimeter. By measuring the forward *I-V* characteristics below 1 V, we could safely neglect the I_1 diffusion current component. We concentrated on separating out the area- and perimeter-related recombination current contributions.

The current-voltage curves on three different diode diameters are shown in Fig. 3. The data are reasonably well represented by a diode quality factor $n = 2$, for both the oxide-coated perimeter and the As_2S_3 glass-coated perimeter. The oxidized perimeter was created by the 1:8:500 (H_2SO_4:H_2O_2:H_2O) etch, which had been used to lithographically define the mesas. Current flow on the As_2S_3-passivated diodes is markedly reduced from the oxide-covered diodes in Fig. 3. This shows that, even for 500 μm diameters, perimeter currents were a dominant contribution to the oxide-coated diodes in this range of bias. Naturally, such current leakage would be even more severe in smaller diodes.

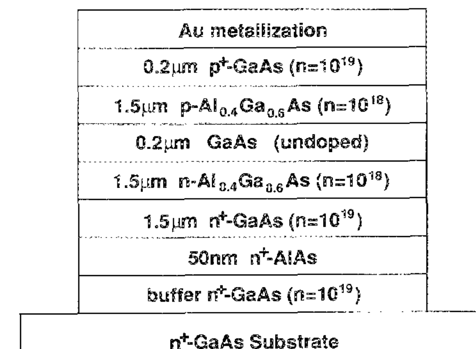

FIG. 2. Mesa diode on which the current-voltage measurements were made, before being coated with As_2S_3.

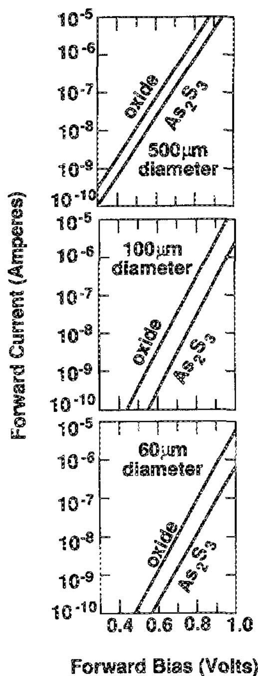

FIG. 3. Forward current-voltage characteristics on mesa diodes of three different diameters. The oxide-coated diodes are dominated by perimeter recombination leakage, while the As_2S_3-coated diodes experience bulk recombination current almost exclusively.

In fitting the curves of Fig. 3, the bulk area-related forward recombination current density, J_{nA}, was taken to be identical for both perimeter compositions. Our best fit for bulk current was $J_{nA} = 7.8 \times 10^{-11}$ A/cm^2. The corresponding determination of the perimeter-related recombination current density on oxide-coated edges was $J'_{nP} = 2 \times 10^{-12}$ A/cm. Within our experimental precision, the perimeter leakage on the As_2S_3-coated diodes was too small to measure! We were only able to place an upper limit on the As_2S_3-coated perimeter leakage current density, which was $J'_{nP} \lesssim 2 \times 10^{-14}$ A/cm, 100 times less than an oxidized GaAs surface.

This As_2S_3 glass coating was recently[13] applied to heterojunction bipolar transistors with a corresponding improvement in electrical characteristics. Our results also have implications for semiconductor lasers and light-emitting diodes. A laser requires a forward bias voltage equal to the band-gap energy, 1.4 eV. At that forward bias the perimeter leakage current on oxidized GaAs becomes $J'_{nP}[\exp(qV/2kT) - 1] \simeq 1$ A/cm of length on the periphery. In semiconductor lasers the lateral edges are frequently resistively isolated from the injection region, but the mirror facets generally experience the full forward injection voltage. A leakage current of 1 A per centimeter of oxidized facet length can contribute noticeably to the threshold current of certain low-threshold lasers. It is possible that a freshly cleaved ⟨110⟩ facet may have less surface recombination. On exposure to air however, it would eventually and inevitably degrade to the level of recombination current we have measured on our oxidized perimeters. These results should stand as a caution to those who model or fabricate semiconductor lasers. If the lateral edge isolation is inadequate, then the laser can draw very large nonradiative currents indeed.

A sensible microscopic model of the perimeter leakage, based upon Shockley–Read–Hall kinetics, is $J'_{nP} = qn_iS_0L$, where q is the electronic charge, n_i is the intrinsic carrier density, and L is the width of the depletion zone on the surface, where $n \sim p$. If the center of the depletion zone is 20 nm wide, then it implies that the flat-band recombination velocity at the oxidized surface is $S_0 = 3.5 \times 10^6$ cm/s. This model would place an upper limit of $S_0 \lesssim 35\,000$ cm/s at the As_2S_3-coated GaAs interface. Such an upper limit is consistent with our direct $S_0 = 15\,000$ cm/s measurement from Fig. 1.

Among the interesting questions, just as for any heterojunction system, is the valence-band offset between As_2S_3 and GaAs. Reference 7 claimed a type II band alignment, although this seems unlikely based on our small measured interfacial recombination velocity.

We have emphasized perimeter passivation on bipolar devices, but there might be metal insulator semiconductor field-effect transistor (MISFET) applications as well. We have made a few such transistors, but we were troubled by pinholes in the insulating As_2S_3 film itself. An auxiliary polyimide layer was needed to prevent pinhole short circuits. The As_2S_3 has[1] a resistivity $\sim 10^{18}$ Ω cm, which is more than adequate. We also made channel conductivity measurements, similar to Ref. 6, finding that the interface charge was $Q = 6 \times 10^{11}$ negative charges per cm^2 in pitch darkness. This level was in between the $(NH_4)_2S$ and $Na_2S \cdot 9H_2O$-coated results in Ref. 6.

As explained in Ref. 1, the As_2S_3 glass tolerates variable stoichiometry. We prepared compositions with a 10% excess of sulfur by including some $(NH_4)_2S$ into the solution of step 5 in Table II. None of the electronic properties which we could measure were affected.

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[1] R. Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983); N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed. (Clarendon, Oxford, 1979).
[2] E. Yablonovitch and T. J. Gmitter, in *Proceedings of the Symposium on Diagnostic Techniques for Semiconductor Materials and Devices*, edited by T. J. Shaffner and D. K. Schroeder (The Elechemical Society, Pennington, NJ, 1988), Vol. 88-20, p. 207.
[3] E. Yablonovitch, D. L. Allara, C. C. Chang, T. J. Gmitter, and T. B. Bright, Phys. Rev. Lett. **57**, 249 (1986).
[4] E. Yablonovitch, C. J. Sandroff, R. Bhat, and T. J. Gmitter, Appl. Phys. Lett. **51**, 439 (1987).
[5] E. Yablonovitch, H. M. Cox, and T. J. Gmitter, Appl. Phys. Lett. **52**, 1002 (1988).
[6] E. Yablonovitch, B. J. Skromme, R. Bhat, J. P. Harbison, and T. J. Gmitter, Appl. Phys. Lett. **54**, 555 (1989).
[7] Yu. G. Fariver, A. I. Bairamov, and T. D. Dzhafarov, Sov. Phys. Semicond. **19**, 795 (1985).
[8] C. J. Sandroff, R. N. Nottenburg, J.-C. Bischoff, and R. Bhat, Appl. Phys. Lett. **51**, 33 (1987).
[9] P. D. DeMoulin, S. P. Tobin, M. S. Lundstrom, M. S. Carpenter, and M. R. Melloch, IEEE Electron. Device Lett. **EDL-9**, 368 (1988).
[10] H. Brugger and P. W. Epperlein, Appl. Phys. Lett. **56**, 1049 (1990).
[11] H. Kawanishi, H. Ohno, T. Morimoto, S. Kaniewa, N. Miyauchi, H. Hayashi, Y. Akagi, Y. Nakajima, and T. Hijikata, SPIE Proc. **1219**, 31 (1990).
[12] T. B. Stellwag, M. R. Melloch, M. S. Lunstrom, M. S. Carpenter, and R. F. Pierret, Appl. Phys. Lett. **56**, 1658 (1990).
[13] H. L. Chuang, M. S. Carpenter, M. R. Melloch, M. S. Lundstrom, E. Yablonovitch, and T. J. Gmitter, Appl. Phys. Lett. **57**, 2113 (1990).