# Nearly ideal electronic properties of sulfide coated GaAs surfaces

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We have discovered that a class of inorganic sulfides [$Li_2S$, $(NH_4)_2S$, $Na_2S \cdot 9H_2O$, etc.] imparts excellent electronic properties to GaAs surfaces. The surface recombination velocity at the interface between $Na_2S \cdot 9H_2O$ and GaAs begins to approach that of the nearly ideal AlGaAs/GaAs interface. We propose the formation of a robust covalently bonded sulfide layer to explain the favorable electronic quality of such interfaces.

From the earliest days of solid-state electronics it has been recognized that surfaces and interfaces are playing a decisive role. Indeed the discovery of the first transistor,[1] the point-contact transistor, was critically dependent on the favorable surface recombination velocity (SRV) of germanium. Recently there has been an upsurge of scientific interest in the artificial synthesis of electronically ideal semiconductor surfaces by chemical,[2] photochemical,[3] and physical[4] means. From the point of view of electronics, it is desirable to covalently satisfy *all* surface bonds, thereby shifting the surface states out of the band gap and into the valence and conduction bands.

Electronic devices can be uniquely sensitive to electrically active surface sites even at a level of a part per million. SRV is a good means of parametrizing such surface quality. We have discovered that a class of inorganic sulfides [$Li_2S$, $(NH_4)_2S$, $Na_2S \cdot 9H_2O$, etc.] imparts excellent electronic properties to GaAs surfaces. The SRV at the interface between $Na_2S \cdot 9H_2O$ and GaAs begins to approach that of the nearly ideal AlGaAs/GaAs interface. Subsequent to our work this interfacial system has been employed on GaAs heterojunction bipolar transistors[5] to improve the current gain by sixtyfold.

A particularly versatile new probe of SRV is the contactless laser-pumped carrier lifetime bridge. It is an adaptation of an apparatus which had previously been used to elucidate some remarkably long lifetime[2,6-8] recombination properties of silicon and silicon surfaces. The inductively coupled radio-frequency apparatus, illustrated in Fig. 1, monitors the absolute sheet conductivity of the semiconductor as a function of time. A short pulse of incoherent light from a *Q*-switched doubled Nd:YAG laser scattering off a white surface, injects electrons and holes into an AlGaAs/GaAs double heterostructure epilayer. The recombination of electrons with holes is monitored by the decay of the conductivity associated with the optically injected carriers. In a numerical algorithm, conductivity is divided by the carrier-density-dependent mobility to convert it to a density decay curve. 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[1]:

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

where $\tau_b$ is the bulk recombination lifetime, $S$ is the SRV of the front surface which is accessible for chemical modification, and $S_h$ is the almost negligible SRV of the rear AlGaAs/GaAs heterostructure interface. The reciprocal of the quantity in parentheses in Eq. (1) was called by Shockley[1] the "filament lifetime" $\tau$, 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 $L < \sqrt{D\tau}$ where $D$ is the ambipolar diffusion constant and $\sqrt{D\tau}$ is the diffusion length.

At the heart of these experiments is a particularly high-quality, 7-$\mu$m-thick, organometallic chemical vapor deposition grown AlGaAs/GaAs/AlGaAs double heterostructure of negligible doping density $\sim 10^{14}/\text{cm}^3$. The initial step entailed measuring the density decay curve of the intact double heterostructure. This is shown in Fig. 2(a). Then the upper AlGaAs layer was selectively etched away exposing the free GaAs surface. Following an interfacial chemical treatment the density decay was measured again on exactly the same sample. The density decay curves for the original intact double heterostructure and a number of chemical preparations are shown in Fig. 2. The initial nonexponential character of the double heterostructure decay curve is due to the influence of bulk Auger and radiative recombination. By employing the intact double heterostructure decay curve as a reference we can subtract out the effect of bulk recombina-

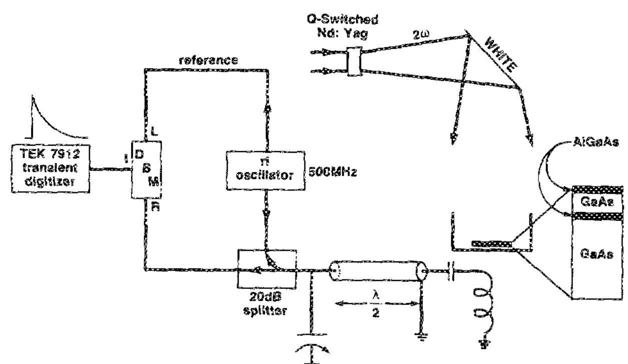


FIG. 1. Doubled Nd:YAG laser scatters off a white surface and injects carriers into a GaAs double heterostructure epilayer. The transient conductivity is probed by rf induction at 500 MHz. The series resonant circuit, adapted from NMR technology, includes a $\lambda/2$ section of co-ax for convenient 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. The AlGaAs layer is then removed and the experiment repeated with a wide variety of possible surface treatments.

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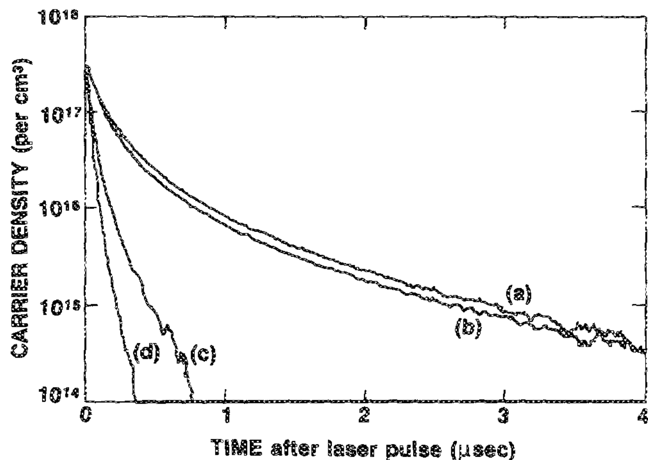


FIG. 2. Decay of carrier density in a GaAs double heterostructure excited by delta function optical injection at $t = 0$: (a) AlGaAs/GaAs; (b) $Na_2S \cdot 9H_2O$/GaAs; (c) photochemical treatment (Ref. 3); (d) clean GaAs surface exposed to air.

tion leaving only the difference in SRV between the AlGaAs/GaAs 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 AlGaAs/GaAs interface is $(S - S_h)/L$. Since $S_h$ is generally thought to be negligible, with an upper limit[9] $\leqslant 450$ cm/s, the result is a measurement of the density dependence of the SRV of the chemically prepared GaAs surface. For the sake of definiteness we took $S_h = 50$ cm/s in our data analysis.

Returning now to Fig. 2, we can compare the decay curves resulting from a number of chemical procedures with that obtained for the AlGaAs/GaAs heterostructure, considered to be an ideal electronic interface. The lowest curve (d) representing the surface with the poorest electronic quality is for a GaAs surface which was chemically etched in 1:8:500 ($H_2SO_4$:$H_2O_2$:$H_2O$), rinsed in distilled water, then dried in air. The measured $S$ was $\geqslant 25\,000$ cm/s, at the upper limit of our dynamic range for this sample thickness. Curve (c), also measured in air, is the result of a recently introduced[3] photochemical surface preparation and $S$ was found[10] to be reduced to $\sim 10\,000$ cm/s. The decay curve (b) shows the effect of depositing thin films of $Na_2S \cdot 9H_2O$ onto GaAs surfaces cleaned as in (d). A typical deposition procedure involved spin-on at 5000 rpm using a 1-M aqueous solution of the salt, which left behind a dry polycrystalline film $\sim 1\ \mu m$ thick. As a result of our $Na_2S \cdot 9H_2O$ coating $S$ has been reduced to $\sim 1000$ cm/s and the density decay curve lies only slightly below that of the intact double heterostructure shown in curve (a).

If we make the usual simplifying assumptions that $S = N_t v_{th} \sigma$, where $N_t$ is the surface density of recombination centers, $v_{th} \cong 10^7$ cm/s is the carrier thermal velocity, and $\sigma \sim 10^{-15}$ cm$^2$ is the recombination cross section, then the low $S$ for the GaAs surface coated with $Na_2S \cdot 9H_2O$ implies $N_t \sim 10^{11}/\text{cm}^2$. In other words there is only one electronically active surface defect out of every $10^4$ surface bonds.

A careful analysis of the carrier density dependence of SRV for all the different preparation methods shows that $S$ is highest at the highest carrier densities and experiences its lowest values at the lowest carrier densities. An example of this is shown in Fig. 3. This is the classical behavior to be expected in the presence of surface fixed charge. In general the effects of band bending on SRV are very complex and require the introduction[7] of the concept of a "generalized SRV." Our case, of negligible background doping and high level injection $n \cong p$, permits some simplifications: The effect of fixed charge is to bend the bands so as to repel whichever carrier has the least probability of being near the surface. In Shockley–Read–Hall recombination the capture of minority carriers is the rate limiting step. Therefore, so long as $n \cong p$ in the bulk, band bending always acts to diminish the $S$ from what it would be otherwise:

$$S = S_0 \exp(-|\varphi|/kT), \tag{2}$$

where $S_0$ is the SRV in the absence of band bending, $kT$ is thermal energy, and $\varphi$ is the band bending. This model assumes that the cross-section ratio[7] for capturing holes versus electrons does not differ too greatly from unity. For a given surface fixed charge $N_{ss}$ the amount of band bending can be determined from the nonlinear solution of the Poisson–Boltzmann equation:

$$\frac{2\pi N_{ss}^2 q^2}{\epsilon kT} = p(e^{-\psi} + \psi - 1) + n(e^{\psi} - \psi - 1), \tag{3}$$

where $q$ is the charge of the electron and $\epsilon$ is the dielectric constant of the semiconductor, $\psi = \varphi/kT$, and $n$ and $p$ are the bulk values. The experimentally observed density dependence of $S$ can then be fit using $N_{ss}$ as the adjustable parameter. For the $Na_2S \cdot 9H_2O$ coating in Fig. 3 a surface fixed charge of $2\times 10^{11}/\text{cm}^2$ and an $S_0$ of 9000 cm/s were needed to fit the observations. In other words the reduction of $S_0$ to 9000 cm/s is a measure of the surface electronic quality and the further reduction of $S$ to 500 cm/s at $n \sim 5\times 10^{15}/\text{cm}^3$ is due to a repulsion of minority carriers by a 75-meV potential. For other surface preparations $N_{ss}$ varied from $5\times 10^{10}$ to $2\times 10^{11}/\text{cm}^2$ with generally higher $S_0$. We note that the concept of Fermi level pinning need not really apply to a forward biased or optically injected semiconductor since the carrier density itself will tend to flatten the bands.

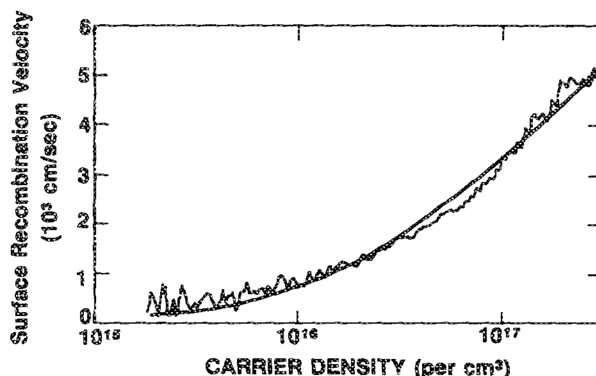


FIG. 3. Variation of $S$ with optically injected carrier density for $Na_2S \cdot 9H_2O$/GaAs. At high density the bands tend to flatten as the surface charge is screened out. At low density, minority carriers are repelled from the surface, reducing $S$. The solid line is a theoretical curve for $N_{ss} = 2\times 10^{11}$ charges/cm$^2$, and $S_0 = 9000$ cm/s.

We believe that the chemical reaction mechanism responsible for the low $S$ at the $Na_2S \cdot 9H_2O$/GaAs interface can be explained by a two-step process where the GaAs surface is first etched clean yielding a pristine surface to which sulfur can form strong, covalent, chemical bonds. The first step, chemical etching, is presumably accomplished through the joint action of hydroxide and sulfide ions which are present in the aqueous ($p$H ~ 12) sulfide solutions. Interestingly, the wafer immersed in aqueous base ($NH_4OH$, NaOH, KOH, etc.) gave $S$ almost as favorable as the $Na_2S \cdot 9H_2O$ coating. Several models suggest that surface oxides in the form $As_2O_3$ and $Ga_2O_3$ together with elemental arsenic are responsible for the high concentration of mid-gap defects associated with the GaAs surface. In this context we expect that our aqueous alkaline environment aids in the dissolution of any surface oxides while sulfide ions react with elemental arsenic to form any one of a number of highly soluble sulfur complexes. This etching mechanism is quite similar to the one proposed[11] to account for the favorable effects of aqueous solutions of $KOH/K_2Se$ on GaAs and is consistent with previous work showing that clean GaAs surfaces possess superior electronic properties.

Though ridding the GaAs surface of oxides and arsenic can result in dramatically improved surface properties, in order to achieve long-lived surface passivation it is necessary to form a chemically resilient surface layer which is stable against reoxidation in air. In Fig. 4 we illustrate the robust nature of our thin sulfide films by following the effect of various post treatments on $S$. Curve (a) is the density decay measured from a GaAs surface with a freshly spun film of $Na_2S \cdot 9H_2O$ with $S \sim 1000$ cm/s. After annealing at 150 °C for 1/2 h in a $N_2$ atmosphere, curve (b) reveals that $S$ rose to ~1500 cm/s. We have heated to temperatures as high as 350 °C observing the same qualitative trend. In curve (c) we can see the effects of leaving the films exposed to air for 19 h at room temperature. Though $S$ has climbed to ~3000 cm/s, it is still remarkably good. Finally, curve (d) shows the effects of a thorough water rinse on the annealed sample (b). At this point $S$ has been increased to ~5000 cm/s, a value comparable to that of photochemically treated GaAs.

To rationalize the long-lasting electronic benefits of $Na_2S \cdot 9H_2O$ films deposited on GaAs, we speculate that a robust chemically bound sulfide layer forms on the surface. Preliminary Auger analysis on films which were heated then rinsed as in curve 4(d) shows that roughly half a monolayer of sulfur is present on the surface with oxygen comprising the rest of the surface layer. It is conceivable, therefore, that the higher $S$ obtained after heating and rinsing the sulfide films results from a surface oxidation reaction which redeposits elemental arsenic on the GaAs surface. Not all of the surface sulfide phase is displaced however, and it might be worthwhile to speculate on its identity.

Sulfur is a versatile element with regard to GaAs and it forms many stable binary compounds with both Ga and As. In fact the chalcogenides have been cited on several occasions[11-13] for being able to lower the surface density of states

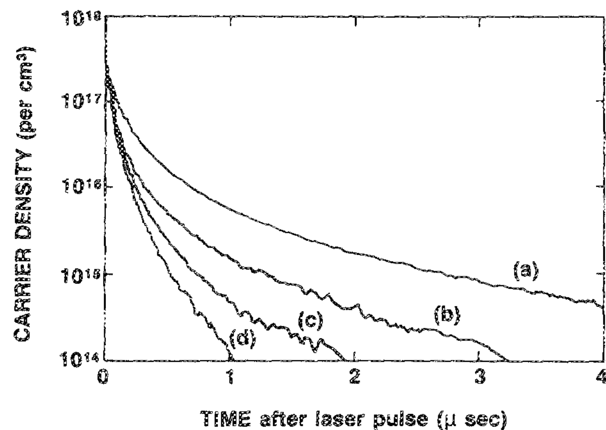


FIG. 4. Effect of aging and annealing on density decay curves: (a) freshly prepared $Na_2S \cdot 9H_2O$/GaAs; (b) annealed at 150 °C for 30 min; (c) aged in air for 19 h; (d) water rinse of the annealed sample (b).

in GaAs, a result presumably of a strong chemical affinity between sulfur and GaAs. In our case it seems plausible to propose that sulfur would bond with surface gallium atoms, since we believe that elemental arsenic is efficiently etched away during exposure to the sulfide solution. The most efficient use of sulfur, which also leaves the surface free of dangling bonds, would have a sulfur atom bridging two surface gallium atoms. From the mechanism we might infer that reoxidation of GaAs takes place by the cleavage of one of the bridging bonds, leaving roughly half the gallium atoms open to attack by oxygen.

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