



Recombination Velocities on GaAs<100> Surfaces Immersed in Aqueous Solutions

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In this note we examine the dependence of the surface recombination velocity (SRV) of n-GaAs<100> on aqueous solution environments, including selenide solutions, and on ruthenium treatment of the surface (1,2,3). We find that SRV is sensitive to pH, presence or absence of O₂, basic Se²⁻, oxidation of the basic Se²⁻ to Se_x²⁻, and Ru³⁺ treatment.

The test sample was an organometallic chemical-vapor-deposition-grown

Al_{0.5}Ga_{0.5}As/GaAs/Al_{0.5}Ga_{0.5}As double heterostructure with a nominally undoped (~10¹⁴cm⁻³) active layer of 2 μm thickness. The experimental system, and data analysis were the same as those described by Yablonovitch (4,5).

For reference purposes, the decay of carrier density of the intact double heterostructure was measured and recorded prior to chemical treatment and is shown in Figure 1(a). The top Al_{0.5}Ga_{0.5}As epilayer was then selectively removed in hydrofluoric acid and the exposed GaAs surface was briefly etched in 1:8:500 (H₂SO₄:H₂O₂:H₂O) followed by a deionized water rinse. Next, the crystal was placed in a teflon cell under nitrogen or air and the particular solution under study was added with a dropper until the entire crystal was covered with liquid. The carrier decay curve was then monitored in situ for each solution and recorded for further data analysis.

Figure 1 shows the decay curves of several surface preparations studied as well as the initial Al_{0.5}Ga_{0.5}As/GaAs/Al_{0.5}Ga_{0.5}As double heterostructure. For the sake of consistency, the same sample was used for all the different surface treatments.

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 (4,5):

$$\frac{dn}{dt} = - \left[\frac{1}{\tau_b} + \frac{S + S_h}{L} \right] n \quad [1]$$

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 almost negligible

SRV of the rear AlGaAs/GaAs heterostructure interface. The reciprocal of the quantity in brackets in eq. (1) was called by Shockley the "filament lifetime" τ, which in general may depend on n (6). 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 ≤450 cm/sec, the result is a measurement of the density dependence of the SRV of the chemically prepared GaAs surface (7). For the sake of definiteness we took S_h = 50 cm/sec in our data analysis.

The non-exponential character of the decay curves 1(b), 1(c), 1(d) and 1(e) indicates the presence of considerable surface charging and band-bending, similar to that previously seen in sulfide coated surfaces (5). This makes the SRV particularly slow at low carrier densities. To reduce the influence of this effect, the values of SRV or S quoted in this article are for a bulk injection level ~10¹⁶/cm³ where band-bending is greatly diminished.

The decay curves illustrated in Figure 1 can be interpreted in terms of the following SRVs: Curve 1(b), Na₂S·9H₂O solid polycrystalline coating, yields S≈600 cm/sec. Curve 1(c) for GaAs<100> immersed in a yellow 0.6M K₂Se/1.0M KOH solution, yields S≈1700 cm/sec. After the same solution was allowed to oxidize in air to dark-brown Se_x²⁻, the SRV increased to S≈8000 cm/sec (curve (d)). Curve 1(e) demonstrates the poor quality (S≥20000 cm/sec) of the 1:8:500 etched starting surface, in air.

The following SRVs were measured in other environments (no decay curves are shown): Air saturated 0.1M HCl; S≥20000 cm/sec; De-oxygenated 0.1M HCl, S≈15000 cm/sec; De-oxygenated 0.1M HCl after immersion in 0.01M RuCl₃/0.1M HCl, S≈10000 cm/sec; Yellow 0.6M K₂Se/1.0M KOH, after immersion in 0.01M RuCl₃/0.1M HCl, S≈13000 cm/sec; Air saturated 1M KOH, S≈3000 cm/sec.

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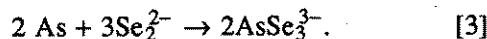
These results indicate that:

- (i) Base strips or shifts the surface states present in acid, reducing SRV.
- (ii) The density of damaging states is greater in oxygenated solutions than in de-oxygenated ones.
- (iii) In de-oxygenated acid Ru^{3+} treatment reduces SRV, though it increases SRV in bases.
- (iv) In basic Se^{2-} solutions SRV is low, approaching those values seen in basic S^{2-} solutions.
- (v) Oxidation of Se^{2-} to Se_x^{2-} substantially increases SRV.

The results are consistent with the suggestion that the damaging surface states are introduced when a reactive surface oxide, containing AsO_3^{3-} or As_2O_3 , interfacially reacts with GaAs to produce excess elemental arsenic (8-11) (i.e., Ga vacancies) by the reaction



In the absence of oxygen the rate of oxide formation is reduced. Furthermore, As_2O_3 , H_3AsO_3 , as well as salts of the H_2AsO_3^- and HAsO_3^{2-} anions dissolve in base, but dissolve less readily in acid. Selenides react with elemental arsenic (9), dissolving it via reductive reactions such as



When Se_2^{2-} is oxidized to higher polyselenides (Se_x^{2-}), i.e. when the solution's redox potential is made sufficiently oxidizing, As may no longer dissolve.

The surface created on GaAs upon reaction with Ru^{3+} in deoxygenated acid is superior to the untreated surface in the same solution, but is inferior to that in base. It is substantially inferior to that in basic selenide. This is consistent with the following hypothesis: The As_2O_3 i.e. H_3AsO_3 containing interface, that is present in acid, might be partially stabilized against reacting with GaAs to form Ga_2O_3 and As (according to reaction 2) after conversion to a ruthenium arsenite (reaction 4).



If the ruthenium arsenite reacts with GaAs, less As is formed in the reaction



than is formed in reaction 2.

In summary, the SRV on GaAs(100) is highly sensitive to pH, to the presence of oxygen, to surface treatment with Ru^{3+} , and varies with the oxidation state of selenide/polyselenide ions.

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Manuscript received May 4, 1988.

AT&T Bell Laboratories assisted in meeting the publication costs of this article.

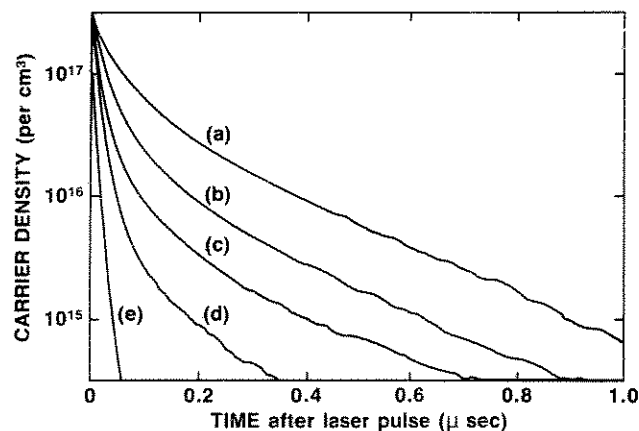


Figure 1. The decay of carrier density in a GaAs double heterostructure excited by delta function optical injection at $t=0$. (a) AlGaAs/GaAs. (b) $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}/\text{GaAs}$. (c) Aqueous solution 0.6M K_2S , 0.0M KOH. (d) Same solution oxidized to Se_2^{2-} . (e) Clean GaAs surface exposed to air.