MINORITY CARRIER LIFETIME OF HETEROSTRUCTURES, SURFACES, INTERFACES AND BULK WAFERS

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ABSTRACT

We have developed a contactless laser-pumped minority carrier lifetime probe which is of general utility in semiconductor electronics. We have employed this inductively coupled radio frequency probe to study: epitaxial heterostructure quality for different growth methods; wafer substrate quality; interfacial recombination; chemical synthesis of nearly ideal electronic surfaces; radiative electron-hole recombination; "naked" quantum wells; heterojunction bipolar transistors; and rapid contactless monitoring of semiconductor process development.

Since the pioneering work of G. L. Miller (1), it has been known that virtually every electrical measurement on semiconductors can be implemented by contactless inductive coupling, i. e. without the need for actual physical wire contact. We will be describing contactless radio frequency bridges which can measure dc conductivity and pulsed photoconductivity of semiconductors. Sophisticated contactless measurements, with no need for standard device processing, allow rapid monitoring of: epitaxial heterostructure quality for different growth methods (2); wafer substrate quality; interfacial recombination (3); chemical synthesis of nearly ideal electronic surfaces (4); radiative electron-hole recombination; "naked" quantum wells (5); heterojunction bipolar transistors (6); and rapid contactless evaluation of semiconductor process development (7).

A block diagram of the inductively coupled radio frequency bridge, suited for Silicon work, operating at 70 MHz is shown in Figure 1. A similar laser pumped apparatus, designed for the higher speeds of III-V semiconductors, operating at 500 MHz is shown in Fig. 2. This inductively coupled radio frequency apparatus monitors the absolute sheet conductivity of the semiconductor, both dc and pulsed.

The heart of the system is a 3 to 5 turn radio coil about a centimeter in diameter. In effect the coil is the primary of a transformer, and the semiconductor wafer is a one turn secondary. The effective resistance in the secondary circuit will be boosted by the turns ratio squared when monitored in the primary circuit. If we approximate the secondary circuit resistance as the sheet resistance of the semiconductor wafer, then a sheet resistance of 100 Ohms per square will look like ~1000 Ohms in parallel with the primary. The rf bridge is balanced when the primary circuit is matched to 50 Ohms by the fixed and the variable tuning capacitor. Small sheet conductivities will only perturb the tuning, and the reflected rf wave from the primary coil will be linearly proportional to sheet conductivity of the semiconductor wafer. However a sheet conductance as high as ~0.2 Mhos per square in the secondary will look like ~50 Ohms in the primary and will exceed the linear dynamic range of the circuit.

The circuits are designed to digitize the reflected rf signal due to the impedance imbalance caused by the sheet conductivity of a semiconductor wafer. If known calibration wafers are repositioned to the exact same geometry, then the bridge signal can be calibrated absolutely in Ohms per square. In effect we have a very fancy, inductively coupled, time resolved, Ohm-meter. The actual circuits shown in Figures 1 and 2 were adapted from those radio circuits used in Nuclear Magnetic Resonance (8).

When the rf bridge is operated in the photoconductivity mode it can be a particularly valuable probe of minority carrier properties. A brief flash of pulsed incoherent light, from either a strobe lamp or a Q-switched doubled Nd-Yag laser scattering off a white surface, injects electrons and holes into an epilayer or into a bulk substrate wafer itself. 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 (9):

$$\frac{dn}{dt} = -\left[\frac{1}{\tau_b} + \frac{2S}{L}\right] n$$

where τ_b is the bulk recombination lifetime, S is the surface recombination velocity, and the factor 2 accounts for the front and back surfaces. The reciprocal of the quantity in brackets was called by Shockley (9) 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. If the front and back surfaces of the epilayer are inequivalent then $(S_f + S_b)$ should be substituted for 2S.

In this paper we will review the operation of the minority carrier lifetime bridge and show how it can be a real workhorse in the laboratory environment. The main advantage of this equipment is that it can give immediate answers about the semiconducting quality of unprocessed or partially processed materials. We will examine the utility of this type of apparatus by reviewing some of the applications where it was found useful.

EPITAXIAL QUALITY:

The first application will be to compare (2) the quality of III-V double heterostructures which are grown by the three most common growth methods: organo-metallic chemical vapour deposition (OMCVD), liquid phase epitaxy (LPE) and molecular beam epitaxy (MBE). In making these comparisons, it is significant that the epitaxial layers are not subjected to any processing after growth. Because there are no contacts required, we see the material quality directly as grown. The best and most consistent minority carrier properties came from OMCVD, but the other growth methods were almost as good. Figure 3 shows the decay of minority carrier density of one of the better OMCVD double heterostructures that we had tested. The initial decay at high densities is due to radiative and Auger recombination. The long exponential tail at low density is due to Shockley-Read-Hall recombination which is defect sensitive. Typically τ_{SRH}, the Shockley-Read-Hall lifetime, was 1 to 2 μsec for OMCVD material, 0.5 to 1 μsec for LPE material and 0.25 to 0.5 μsec for MBE material.

These lifetimes are much longer than accepted by conventional wisdom, but they agree with independent measurements (10). Conventional wisdom would have a III-V lifetime of only a few nanoseconds. This erroneous impression is based on: (i) Heavily doped (10^{18} /cm^3) or highly injected material in which Auger and radiative recombination are fast. (ii) Bare GaAs rather than double heterostructure material in which the surface recombination is prevented. (iii) Substrate quality material which is poor rather than epitaxially grown material which is excellent.

The bulk Shockley-Read-Hall lifetime is often expressed as $1/\tau_{SRH} = N_t v_{th} \sigma$. Typical values of the carrier thermal velocity are $v_{th} \approx 10^7$ cm/sec and for the capture cross-section $\sigma \sim 10^{-15}$ cm^2. Then the deep recombination center density N_t would be approximately 10^{14} defects/cm^3 which is a reasonable deep trap concentration for our high quality material. A possible objection to this interpretation of our rather long measured lifetimes is that they may have been increased by the ratio of time spent in traps to the time spent as free electrons. In many dirty photoconductors (11), the shallow trap density is higher than the injection level and the carriers become stored in shallow traps where they neither recombine nor contribute to the conductivity. Then the lifetime is increased by the ratio of the number of trapped electrons to the number of free electrons. There are two reasons why this is not happening here: (1) If a significant fraction, say 10% of the injected electrons were in traps, they could not contribute to the photoconductivity and would present a 10% error in the absolute signal level, which would easily have been detected. (2) The excellent bulk quality ensured that all traps would be saturated at injection levels above $10^{15}/cm^3$. It may be worth noting that Nelson's photoluminescence decay lifetime experiment (10), which does lend itself to absolute calibration, could not rule out the possibility of a shallow trap dominated lifetime.

The long lifetimes measured here show that GaAs material quality need not be a limitation to the performance of electronic devices. In practice however, considerable deterioration arises during device processing and it would be valuable to repeat this type of measurement at each processing step to identify the dangerous step. That will be discussed later in the paper.

SURFACE QUALITY:

The second application we will discuss is the exploration for surface chemical treatments (4) which produce a surface recombination velocity (SRV) which begins to compete, for example, with the excellent AlGaAs/GaAs interface. The minority carrier lifetime bridge is a superb exploratory tool since different chemical preparations can be tried one after the other with no special device fabrication in between. A "cut and try" approach makes sense if we can try many different chemical reagents in a brief time. Then we can quickly converge on a good chemical process by trying many different variations on any approach that seems to work well. The best chemical treatments so far: For GaAs, a polycrystalline film (4) of $Na_2S{\cdot}9H_2O$; For $In_{0.53}Ga_{0.47}As$, a polycrystalline film (5) of NaOH; For Silicon, treatment in (4) HF acid. The respective carrier density decay curves are shown in Figures 4, 5 and 6. Fig. 4 compares the density decay in a GaAs double heterostructure excited by delta function optical injection at $t=0$ for four different surface treatments: (a) AlGaAs/GaAs. (b) $Na_2S{\cdot}9H_2O$/GaAs. (c) Photochemical treatment (12). (d) Clean GaAs surface exposed to air. The $Na_2S{\cdot}9H_2O$/GaAs surface has led to high gain heterojunction bipolar transistors (6) in which the current gain was increased from $\beta \sim 30$ to $\beta \sim 2000$. As was well known from the first bipolar transistors (9), they are acutely sensitive to surface quality.

Fig. 5 compares four different surface treatments on $In_{0.53}Ga_{0.47}As$ 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 10M NaOH/$In_{0.53}Ga_{0.47}As$ after 30 min. at T=20°C. (c) Spun dry NaOH/$In_{0.53}Ga_{0.47}As$. (d) Native oxide/$In_{0.53}Ga_{0.47}As$. It should be remarked that the surface quality of $In_{0.53}Ga_{0.47}As$ before special chemical treatment is superior to GaAs with the best chemical treatment ($Na_2S{\cdot}9H_2O$) we know. The remarkably favorable surface quality of $In_{0.53}Ga_{0.47}As$ lends itself to the formation (5) of "naked quantum wells" in which one face of the quantum well is exposed.

Fig. 6 shows the carrier density decay from a particularly long lived sample of float-zone Silicon which had been chemically oxidized and then tested in Hydrofluoric Acid. The time scale is tens of milliseconds rather than the microseconds or less for the III-V semiconductors. The difference is not simply due to the contrast between direct and indirect gap materials. In fact the quality of the best float-zone Si is 10^4 better than the best III-V epitaxial material. This can be translated into the number of Shockley-Read-Hall defects/cm^3. Where previously we discussed 10^{14} defects/cm^3 for GaAs, we must now speak of 10^{10} defects/cm^3 for selected float-zone Silicon. Since the HF treatment is so easy, it is straightforward to survey many different batches of Silicon to find the better ones.

Such a good bulk lifetime can only be monitored in the presence of an excellent SRV. The surface quality can be separated out by comparing different thicknesses as the same sample is etched down. This is shown in Fig. 7. The slope gives the SRV which was around 0.25 cm/sec for Si<111>. A summary of everything we have learned about SRV in the major semiconductors is graphically illustrated in Fig. 8. When the surface is at its worst SRV $\sim 10^7$cm/sec in all cases. The best SRV of any semiconductor interface is HF treated Si<111>. All the other surface treatments fall somewhere in between.

BULK WAFER QUALITY:

A by-product of the capability to create a nearly ideal semiconductor surface chemically, is that it allows us to eliminate the surface as a problem in order to focus in on bulk quality. Therefore we have looked at the bulk minority carrier lifetime of substrate wafers whose surfaces had been chemically treated to effectively eliminate surface recombination. The conclusion is that bulk III-V wafer material never seems to have a lifetime longer than 10 or 20 nsec, while epitaxial material grown on those wafers can be as much as 100 times better. Similarly we surveyed bulk Silicon wafers and found that commercial float-zone Silicon is sometimes as good as 40 msec as shown in Fig. 7 but that Czochralski material is generally about 1000 times worse.

I should emphasize that these measurements are taken on essentially unprocessed wafer material. The results could be worse as a result of thermal processing. This suggests the use of the lifetime bridge as a process monitor. Since it requires no special wafer processing itself, contactless lifetime monitoring is excellent for before/after tests. We have used it to make seemingly minor, but critical adjustments in Silicon oxidation conditions (2) to sustain minority carrier lifetime in oxidized float-zone material. Likewise, we have used it to perfect the process conditions (7) for minimizing the forward leakage current of SIPOS heterojunction contacts on Silicon.

We have tried to show that contactless minority carrier lifetime measurement with the photo-pumped rf bridge can be an indispensible tool in any semiconductor laboratory. In conjunction with some of the chemical surface treatments its analytical capabilities extend over a broad range of processed and unprocessed semiconductors.

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