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The Effect of Process Conditions on the Performance of Epitaxial InP Solar Cells*

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Introduction

Indium phosphide solar cells have a higher resistance to electron irradiation than Si or GaAs cells of comparable junction depths [ref. 1, 2]. As a result, there is much interest in the use of this material for space applications. Cells of this material have been made in bulk InP by a number of techniques, including ion implantation [ref. 3], direct diffusion in sealed ampoules [ref. 4] and by open tube diffusion methods [ref. 5]. However, it is generally considered that the epitaxial approach will be superior to all of these techniques.

The epitaxy of Indium Phosphide is considerably more difficult than that of gallium arsenide, for a number of reasons. Perhaps the most important is the fact that the native oxides of In are extremely difficult to remove, as compared to that of Ga. In addition, thermal treatments for the desorption of these oxides often result in the formation of phosphorus vacancies and free indium on the surface. Thus, inadequate sample preparation before epitaxy, poor reactor cleaning procedures, or poor transition procedures between the growth of successive layers, all give rise to trap phenomena and to high interface recombination velocities. Moreover, the lifetime of the grown material is dominated by the occurrence of native defects, so that it is a strong function of growth parameters.

These problems are of special interest to the fabrication of solar cells, where long lifetime, combined with the absence of traps, is highly desirable. This paper describes a study of this problem, using a non-invasive diagnostic technique which we have developed.

Technical

InP layers were grown at atmospheric pressure in a horizontal reactor with an r.f. heated susceptor. The reactor tube was 50 mm in diameter, and all flows were set by mass flow controllers. Semi-insulating (100) InP substrates, misoriented 2° → (110) were used for this study.

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Growth was carried out by the simultaneous pyrolysis of trimethylindium (TMIn) and phosphine gas, with a TMIn partial pressure of 0.042 Torr. The partial pressure ratio of PH_3/TMIn, referred to as the V/III ratio, was varied from 70 to 210 for this study. For these conditions, the growth rate was 1.5 μm/hr.

Lifetime and trapping phenomena were studied by analysis of photoconductive decay transients. In this method, excess carriers are generated by irradiating the sample with light of short wavelength, so as to produce hole-electron pairs. Since the conductivity of the sample is proportional to the total number of carriers, monitoring the conductivity decay after the light is turned off allows the determination of the lifetime.

We have developed a non-destructive method for performing this function, using time domain microwave reflectance spectrometry. Details of this system have been described elsewhere [ref. 6]. In summary, the block diagram of Fig. 1 shows that it consists of four subsystems: a microwave bridge, a pulsed light source for creating the excess hole-electron pairs, a mechanical stage for positioning the sample with respect to the incident RF wave and a data acquisition system. The main components of each subsystem are now described.

The microwave bridge operates at K_a-band (26-40 GHz) and consists of a Gunn oscillator, isolator, attenuators, directional couplers, magic-T, precision sliding short and attenuator, detectors and a few sections of K_a-band waveguide to assemble the bridge. The RF wave is directed to the sample by using a parallel plate antenna which confines and directs the RF wave to a small region of the sample.

The light source for generating the excess carriers is a pulsed GaAs or AlGaAs laser diode with an optical fiber attached to it. This source is used with a generator with a fast decay time to allow measurement of lifetimes as low as 3 nsec.

The mechanical stage is used for positioning the sample with respect to the light beam or the RF wave. The probed region of the sample is defined by the optical fiber which is 0.1 mm in diameter. By using micropositioners, it is possible to do spatial probing of the sample.

The data acquisition system allows saving and analyzing the photoconductivity decay transients for determining excess carrier lifetime. The main components are a digital oscilloscope with at least 100 MHz bandwidth and a low noise wide band amplifier. A computerized analysis of the data is used to extract the appropriate lifetime values.

Figure 2 shows a detailed plot of a typical transient measurement made with this system, averaged over 256 traces to extract the signal from the noise. This characteristic did not change under flood illumination, indicating that the layer is trap free. Computer analysis of this transient resulted in a bulk lifetime of 30 nsec, and a surface recombination velocity (SRV) of 3000-5000 cm/sec.

Results

Effect of HCl Cleaning of the Reactor:

Our reactor cleaning procedure involves a HCl clean of the reactor prior to each growth. This is done by flowing HCl through the reactor with the susceptor held at 1050°C, followed by a bakeout at 1100°C in H_2 gas for two hours. The substrate is loaded after reactor cool down to room temperature, and growth started shortly thereafter.

Figure 4 shows the microwave reflectance transient in the absence of this susceptor clean step. For this sample, strong evidence of traps is observed in the change of transient decay behavior upon flood illumination. From analysis of the transient, the trap lifetime was 1.19 μsec. Trapping phenomena were greatly reduced (but not eliminated) in layers grown after the HCl clean step, as seen from Fig. 5. Here, the trap lifetime, as obtained from an analysis of the transient, was 0.98 μsec.

Effect of an HCl Dip Prior to Growth:

Our cleaning procedure prior to epitaxy is as follows: the substrate is washed in hot organic solvents, followed by a soak in concentrated H_2SO_4. Next, it is rinsed in deionized water and then in methanol. This is followed by a Br-methanol etch step, and a rinse in hot methanol. Additionally, the InP substrate is given a 30 sec. dip in 5% HCl, just prior to loading into the reactor.

Results for two InP layers, grown side by side, are given in Table I, to illustrate the effect of this pre-growth step. The use of this step is seen to greatly improve the minority carrier lifetime, and to completely eliminate traps in the growing layer. The signal amplitude also increased as a result of the lifetime improvement.

Effect of Changing the V/III Ratio:

A series of runs were made at 625°C, with V/III ratios of 70, 140 and 210. In all cases, a pre-cleaned reactor was used, together with a substrate dip in HCl prior to epitaxy. Microwave reflection measurements indicated a bulk lifetime of approximately 30 nsec for all of these layers. We conclude, therefore, that the lifetime is relatively independent of the V/III ratio.

Effect of Growth Temperature:

A number of runs were made with a V/III ratio of 210, and growth temperatures from 600 – 650°C. All samples were treated with the HCl dip before loading in a pre-cleaned reactor, and all were grown with a TMIn partial pressure of 0.042 Torr.

Results of this experiment are presented in Table II. No traps were seen in any of the samples. However, the lifetime was seen to be a strong function of growth temperature, and peaked at 625°C. It should be emphasized that this temperature is machine specific, i.e., it is related to our system configuration and thermocouple placement.

Table II also shows the long wavelength (800 nm) internal quantum efficiency (IQE) of solar cells made at these growth temperatures. All cells were 0.25 cm × 0.25 cm, and were grown on p^+-doped InP substrates. The cell structure consisted of a 0.5 μm p^+-buffer, followed by 3.5 μm p-base and a 500 Å n^+-emitter. In all cases, the reactor was HCl cleaned, and samples were given a short HCl dip, prior to epi-growth. As seen, the IQE peaks for cells grown at 625°C.

Discussion

The effects of process conditions described here can be explained by noting that the electronic properties of InP, grown by organometallic vapor phase epitaxy (OMVPE) are dominated by its defect structure. The starting chemicals, in contrast, are relatively pure except in isolated cases.

DLTS studies made on material grown by OMVPE [ref. 7] show four electron traps, at E1 (0.23 ± 0.03), E2 (0.29 ± 0.03), E3 (0.38 ± 0.04) and E4 (0.61 ± 0.04) eV respectively. Of these, the last has been attributed to iron, which is present in bulk material as well as in semi-insulating substrates which are intentionally Fe-doped. The precise nature of the other three is not known, but is generally associated with phosphorus vacancies and V_p-complexes. They are also observed in MBE-grown material [ref. 8]. All of these defects are of comparable concentration and capture cross section, and reduce the minority carrier lifetime in InP.

As observed earlier, the surface of InP, even after an etch procedure, is covered with a thin film of native oxide. This surface oxide is non-stoichiometric, and is not fully understood at the present time [ref. 9]. Its removal, by thermal treatment prior to epi-growth is not complete; additionally, there is preferential loss of phosphorus during this process. The presence of these residues initiates the formation of defects which propagate through the growing layer.

The HCl dip prior to growth leaves the surface with a strongly adsorbed chlorine layer. The HCl reactor clean step, by the same time, results in adsorbed chlorine on the reactor walls. We propose that, at growth temperatures this reacts with these surface residues, and facilitates their removal via halide formation.

The behavior of El, E2 and E3 each exhibits a pronounced maximum with increasing growth temperature, and then rises sharply. This, in turn, results in a minority carrier lifetime which peaks at some specific growth temperature.

The relative independence of the lifetime with V/III ratio, as well as the sharp maximum with growth temperature, can probably be explained if we assume that these defects are due to V_p and V_p-complexes. Two effects are present with increasing temperature. First, PH_3 is extremely stable, and is not fully cracked until 700°C. Thus, we can expect the pressure of phosphorus over InP to increase exponentially with temperature resulting in a correspondingly rapid *fall* in the native defect concentration. On the other hand, the thermally generated $[V_p]$ can be expected to *increase* exponentially (for constant phosphorus pressure). The presence of these competing effects can explain the observed temperature behavior of lifetime.

In our experiments we have used V/III ratios from 70 to 210, i.e., a relatively small 1:3 range. From equilibrium thermodynamics, this represents a change in $[V_p]$ by a factor of 1.73 assuming P_2 species, and 1.32 assuming P_4 species. These relatively small changes are within the accuracy of lifetime measurement. As a result, the lifetime is relatively independent of V/III ratios for this study.

Conclusion

We have used time domain reflectometry to study the effect of process conditions on lifetime in epitaxial InP. The importance of HCl clean steps, and of reactor temperature have been identified by this technique and verified by measurements of the quantum efficiency of solar cells. A theory, based on the role of V_p and V_p-complexes, has been proposed to explain these results.

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TABLE I. EFFECT OF HCl DIP BEFORE EPITAXY

Condition	τ (nsec)	Signal mV	Comment
No HCl dip	3.5	46	Traps (0.95 μsec)
HCl dip	6.2	175	No Traps

TABLE II. THE EFFECT OF GROWTH TEMPERATURE

T_{growth}	Lifetime (nsec)	QE % at 800 nm
$600°C$	19.8	90
$625°C$	30	97
$635°C$	18	87

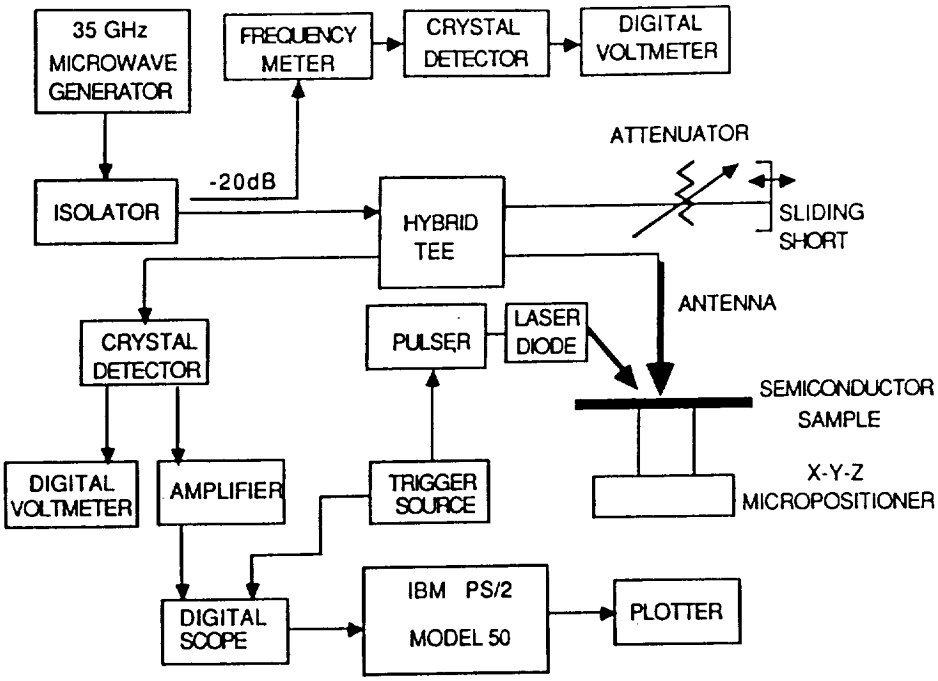

Figure 1. Block Diagram of Microwave Reflectance System.

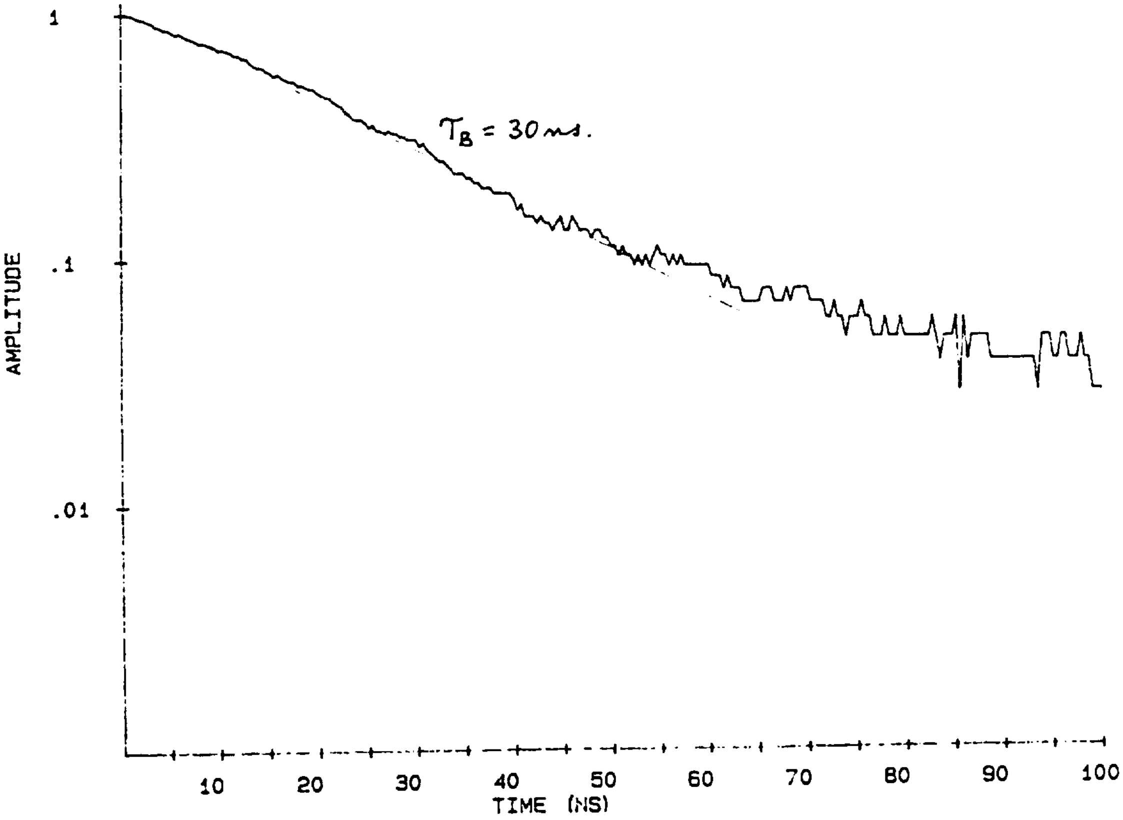

Figure 2. Detail of Transient Response.

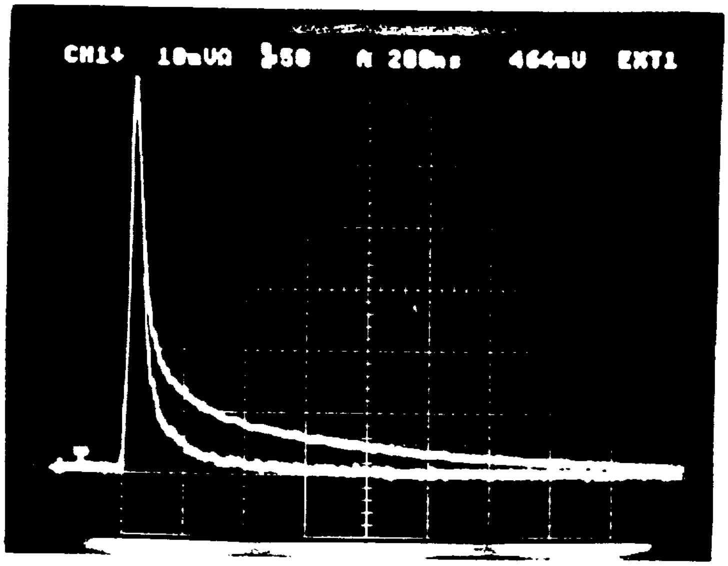

Figure 3. Measurements on a Sample Without Reactor Cleaning (200 nS/div; 10 mV/div).

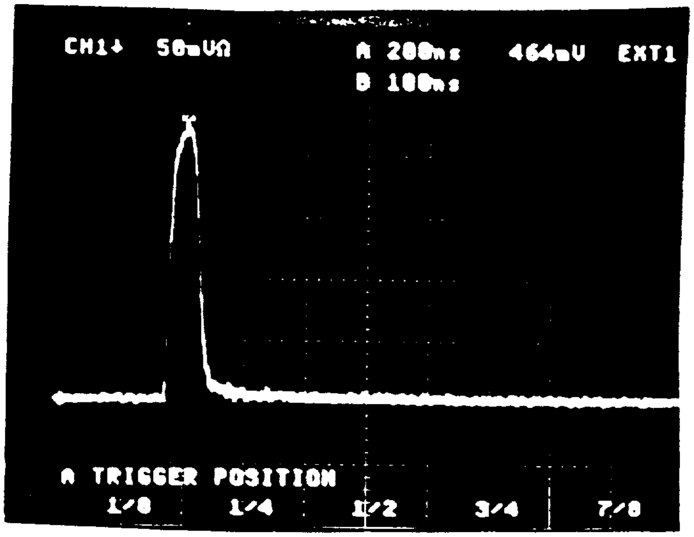

Figure 4. Measurements on a Sample with Reactor Cleaning (200 nS/div; 50 mV/div).