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MICROWAVE OSCILLATIONS IN BULK SEMICONDUCTORS

Fifth Quarterly Progress Report

BY

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For

U. S. ARMY ELECTRONICS COMMAND, FORT MONMOUTH, N. J.

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PURPOSE

The purpose of this contract is to improve the understanding of current instabilities in bulk semiconductors known as the "Gunn Effect" and to investigate the properties of devices employing this phenomenon in order to facilitate an evaluation of their potential as practical microwave circuit elements.

Since this effect depends on the bulk properties of the semiconductor on a microscopic scale, part of this effort will be devoted to the growing and characterizing of high quality intermediate resistivity (1-100 ohm cm) GaAs, either by the controlled addition of dopants or by the annealing of high resistivity material. If the required resistivity can be achieved only by deliberate compensation of donors and acceptors, the problem of obtaining such a balance homogeneously in the material will be investigated.

Although there is now firm evidence that the Gunn effect is a result of intervalley transfer of conduction electrons, a detailed understanding of the mechanism of the instability is not yet available. One approach will be to study the observed "shock waves" of electric field in the bulk of oscillating samples and to explore the effect of material characteristics, applied electric field, and external circuit parameters on its behavior and on the output characteristics of the sample.

Another approach will be to perform diagnostic experiments on oscillating devices in order to understand their performance characteristics and limitations and to determine the underlying causes.

ABSTRACT

Experiments designed to further explore the properties of heat treated boat grown n-type GaAs are described. Doping with radioactive Zn has made possible the determination of the deep donor concentration, yielding a value of $4 \times 10^{16} cm^{-3}$. Material for bulk effect devices is also being obtained by solution regrowth and vapor growth. Efforts to batch fabricate Gunn oscillators with reproducible device characteristics have been disappointing, the source of the problem not yet identified. Experiments designed to measure the drift velocity vs. field in GaAs are underway.

I. MATERIALS STUDIES

A. Introduction

A process for obtaining bulk n-type GaAs of intermediate resistivity has been described in detail in the preceding progress reports. The carrier concentration in this material is fixed by the heat treatment history of the crystal, while the donor distribution is determined by the growth environment. Work has been continuing on the understanding of the details of this process so that material with desired properties can be obtained. In addition it is necessary to characterize the resulting material so that its properties can be correlated with the operating parameters of the resulting devices. An experiment is described below which is designed to measure the density of donor levels in this material. Another experiment is underway to heat treat crystals under different As pressures to determine why and to what extent this affects the properties of the bulk material. In addition work on solution regrowth techniques is being done as an alternative source of intermediate resistivity GaAs.

B. Density of Donor Levels in Oxygen Grown GaAs

As was described in the fourth quarterly progress report, the shallow donor distribution in this material, due principally to Si, is fixed by the growth rate of the crystal, the geometry of the growth vessel, and the initial Ga_2O pressure. In order to measure the density of deeper donor levels an experiment was undertaken to add a radioactive acceptor, Zn, to the crystal growth apparatus. This enables the acceptor concentration in the crystal to be determined by radiotracer techniques, and a measurement of the carrier (hole) concentration yields the donor density from the relation

$$p = N_A - N_D$$

where p is the carrier concentration
N_A is the acceptor concentration
N_D is the donor concentration.

Thus far this experiment has shown that the material is semi-insulating at Zn concentrations less than $3 \times 10^{16} cm^{-3}$. At a Zn concentration of $7.5 \times 10^{16} cm^{-3}$ the material, after a $750^{\circ}C$ heat treatment, is low resistivity p-type and appears to be in carrier exhaustion at room temperature with $p = 3.5 \times 10^{16} cm^{-3}$. Therefore, if the Si concentration is much less than $10^{16} cm^{-3}$ and the Zn concentration is greater than that of any other acceptor level, then N_D is equal to the deep donor concentration and is about $4 \times 10^{16} cm^{-3}$. This indicates, incidentally, that it will be difficult to grow reproducibly p-type GaAs in oxygen with $p < 10^{16} cm^{-3}$ unless some way can be found to reduce N_D.

Now that it has been shown that low resistivity p-type material can be obtained and that the acceptor concentration can be varied, it is hoped that the activation energy of the heat treatable acceptor can be determined.

C. Heat Treatment Under Excess Arsenic Pressure

One crystal was sliced along the growth axis and each half was heat-treated at $750^{\circ}C$, one under the usual Ga rich three phase equilibrium and the other under ten atmospheres of As. Hall Measurements showed no detectable differences between the two pieces but all devices fabricated from the latter piece, as described below, showed very poor characteristics. Whether there is some significant change in the material or whether there was some accident in the experiment is not yet known. This will be repeated and, if the effect is reproducible, steps will be taken to understand what has been changed in the material.

D. Solution Regrown Material

In the second quarterly progress report, an unsuccessful attempt was described to obtain highly doped linear contacts to n-type bulk GaAs by the solution regrowth technique, first described by Nelson.[1] The regrowth was shown to be of good quality but a high resistance interface occurred at the substrate-regrowth interface. Recently Brady et al have reported[2] the successful use of this technique on low resistivity thin epitaxial layers.

Because of the relative simplicity of this process, it is being explored as an alternative source of n-type material for bulk effect devices. This material is the result of adding oxygen grown GaAs to Ga melts which are contained in "Spectrosil" crucibles. The growth occurs after a substrate wafer is dipped into a 900^{o}C melt which is then slowly cooled. So far, attempts to obtain lightly doped n-type regrown material have yielded p-type GaAs with a hole concentration of $2 \times 10^{15} cm^{-3}$ which has been identified as Zn, a shallow acceptor impurity. The properties of the resulting material appears to be independent of the inert flushing gas used.

II. DEVICE STUDIES

A. Introduction

One of the most persistent problems in the device aspect of this program is the fabrication of devices with reproducible properties. In principle this should not be difficult as the structure is simply a semiconductor slab with two electrical contacts. However, we lack a means for characterizing the material on the scale of the device dimensions so we cannot be sure of the suitability of a given piece of material except by fabricating devices out of it. Furthermore, the surface treatment of the material and contact technology is still largely an empirical art rather than a science.

One of the goals of this work is to learn to control these processes so as to produce devices by batch techniques with desirable and reasonably reproducible properties or to understand what the limitations will be and what factors in the material and processes are contributing adversely. Since it is difficult to separate the effects of bulk and contacts on the properties of a single device, we have taken the approach of evaluating contacts by applying them to several types of material and evaluating material by using several contact processes. Results have been rather inconclusive, but it has been clearly shown that the alloyed contacts developed in this laboratory are satisfactory on n-type GaAs with resistivities at least as high as 10 ohm cm and that the heat treated material described in part I produces a high yield of oscillators, at least over the central portion of the crystal cross-section. However, we still cannot confidently attribute the lack of reproducibility of devices to small-scale inhomogeneities in the bulk.

A paper has been submitted for publication which describes the above mentioned contact process including details of the GaAs surface preparation and device fabrication.

B. Vapor Growth of Material and Contacts

As an alternative source of bulk material, a program has been started in this laboratory to vapor grow intermediate resistivity GaAs on semi-insulating and heavily doped substrates using transport mechanisms involving I_2, O_2, H_2O, and $AsCl_3$. In this way we may be able to identify difficulties arising from the heat treat process of the bulk crystals or from surface damage due to polishing of the bulk if significant differences are observed in the operation of devices made from significantly different material.

The material obtained thus far, grown on substrates oriented 5^o off the $\{111B\}$ and $\{100\}$ faces, has not yielded satisfactory devices. Either the device showed a very non-ohmic behavior, or if ohmic, displayed a saturating current characteristic with very weak Gunn oscillations. It is felt that the difficulty is still in the vapor growth process and efforts are being made to improve the system.

We have had some success in vapor growing highly doped layers on n-type substrates by adding Te to the system. If this process can be perfected, it should be possible to make a linear electrical contact to the n-type material; it then becomes much easier to make metallic contacts to the heavily doped layer, as our experience in making injection lasers has shown. This has the advantage that the critical part of the contact process can be done with the same technology and in the same environment as that used for the growth of the material itself. The quality of contacts made by this technique are being evaluated.

C. Devices from Material Heat Treated Under Excess Arsenic Pressure

As was mentioned in part I(A), one crystal was divided in half and these were heat treated at 750^oC, one under standard conditions and one under ten atmospheres of As. The former was used successfully to fabricate high power pulsed devices by P. L. Fleming under another program in this laboratory using alloyed contacts; the latter crystal failed to yield any devices with a well defined threshold and significant oscillation. Care was exercised to control the surface preparation, contact evaporation and alloying. Unless some accident happened in the heat treat process, the addition of the excess Arsenic pressure has a significant effect on the material's suitability

III. MEASUREMENT OF DRIFT VELOCITY IN GaAs

The recent measurement of Gunn and Elliott[3] of the current vs. applied electric field in intermediate resistivity GaAs using fast pulse techniques have indicated that the negative resistance is much smaller than is predicted on the basis of existing theories involving the intervalley transfer of conduction electrons. It was felt that, due to the fundamental importance of the drift velocity vs. field relationship to the understanding of bulk effects, independent measurements should be attempted to confirm this measurement.

Accordingly we have undertaken two types of experiments to accomplish this. Since there is a re-arrangement of fields in the bulk associated with this negative mobility, one must either apply the fields in a time short compared to this re-arrangement time or one must choose a material in which this time is long enough for more conventional techniques to apply. By applying microwave fields of sufficient amplitude one can impose fields in excess of the threshold value fast enough and by injecting carriers into material which cannot easily support domain formation, one can stretch out the re-arrangement time. These experiments are still in their early stages and will be described in later reports.

CONCLUSION

Several techniques are being employed to characterize the heat treated boat grown GaAs used for fabricating bulk effect devices. By doping with radioactive Zinc, it has been shown that the deep donor density is about $4 \times 10^{16} cm^{-3}$. By extension of this technique, it should be possible to measure the activation energy of this level. A preliminary experiment indicates that the properties of the material are grossly affected by heat treating under excess Arsenic pressure although Hall effect measurements show no such effect.

Techniques of solution regrowth, previously explored as a contact process, are now being employed to grow n-type GaAs which will allow controlled comparison with the heat treated material. Initial work has not yet yielded satisfactory growths. A program is also underway to obtain both n-type material and heavily doped contacts by vapor growth. The material so grown has not yielded very satisfactory devices but the contact technique looks promising.

Efforts to obtain devices with reproducible characteristics by batch fabrication have been disappointing. Although we now have confidence in the contact technique, we cannot yet definitely attribute performance variations in devices on microscopic inhomogeneities of the material.

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