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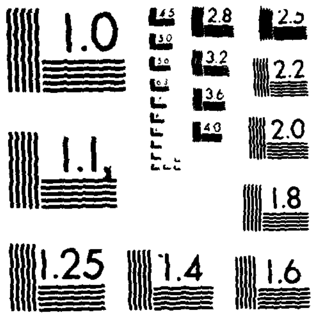
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Final Report (9/30/79)

ONR Contract N00014-76-C-0579

"Insulating Films on GaAs"

Contract Period: 1 March 1976
through 30 September 1979

Total Cost: $156,462

Principal Investigator:
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I. Project Description

This project was an experimental investigation of the formation and the electrical characteristics of thin insulating layers on the compound semiconductor gallium arsenide, GaAs. The primary objective of the study was to obtain fundamental knowledge of the insulator-semiconductor interface for thin film structures formed by two different methods: (1) growth of oxide layers by plasma anodization, and (2) chemical vapor deposition of silicon nitride layers by a low temperature plasma-enhanced technique and a high temperature pyrolytic process. A secondary objective was to develop thin insulating films that may be suitable for surface passivation of GaAs devices.

II. Results of Research

A. Native Oxides by Plasma Anodization.

Thin oxide films have been grown by anodization of GaAs in the negative glow region of a dc oxygen discharge. As-grown and annealed films grown on both p- and n-type bulk GaAs were characterized by conventional electrical measurements and by Auger analysis. The anodic oxide displayed ohmic characteristics up to fields of 0.5×10^6V/cm with a resistivity of $10^{14}\Omega$cm in the as-grown condition and over $10^{15}\Omega$cm after anneal. Capacitance-voltage measurements indicated a fixed positive charge in the insulator of $1.5\times10^{12}cm^{-2}$ for p-type substrates and $4.0\times10^{11}cm^{-2}$ for n-type substrates. Majority carrier trapping near the oxide/GaAs interface was reduced by annealing, and a corresponding reduction of As at the interface was observed. The distribution of fast interface states exhibited a high concentration in the upper half of the GaAs bandgap and a minimum of about 3×10^{12} states/cm^2-eV in the lower half of the bandgap. It was found that excess As at the interface was related to the high interface state density.

B. Plasma Anodization Mechanism

Clean GaAs specimens were plasma anodized sequentially in the two isotopes of oxygen. Subsequent SIMS profiling shows that the last isotope used is dominant in the outermost region of the film. This allows us to rule out interstitial oxygen motion as the dominant mass transport mechanism. More insight into this question was given by experiments in which periods of sputtering were interleaved with periods of anodization. It was expected that the resulting films would be deficient in arsenic since the latter is known to be preferentially sputtered. In fact, the gallium is greatly depleted instead (Ga/As ratio decreased by a factor of 3). This means that the surface of the growing film is normally very Ga-rich and furthermore that Ga is transported through the oxide to react at the surface. Other details of the

Auger profiles suggest that the near-surface region of the growing film is sufficiently different in composition that the As transport mechanism is different there than in the remainder of the bulk.

C. Photoemission Studies of Native Oxide

A sample with a transparent Au top electrode was fabricated in hopes of observing internal photoemission as has been observed in several Si-insulator systems. A measurement of the photon energies required to excite carriers across the interfaces in an MIS device can be used to determine the band gap of the insulator as well as the alignment of the insulator bands with respect to those of the metal and the semiconductor.

Room temperature photocurrent measurements were made at several different biases as a function of photon energy. The photocurrent yield spectra showed modulations in the current due to optical interference effects in the oxide film. The positive and negative Au electrode biases showed the same periodicity, but a reversal of the phase of the modulations. The definition of the modulations was diminished with increased positive or negative bias. The low energy photoemission theshold was 2.25 eV for both bias polarities.

The fact that opposing phases are seen for the two bias polarities indicates that the current generation is near one interface, either the Au or the GaAs, for one polarity while the generation is at the other interface for the opposite polarity. The fact that the photocurrent thresholds are the same for both polarities indicates that the current is due to bulk generation in the oxide rather than to internal photoemission where it is unlikely that identical thresholds would be found. If this is the case, then in order to observe interference effects there must be a highly non-uniform field in the oxide so as to make the drift velocity and, therefore, the contribution to the measured photocurrent larger for carriers generated in the high field region than for those generated in a region of lower field. Preliminary measurements using a low level photovoltage as a measure of transmission of the insulator indicates, for negative Au bias, that the current generation is near the Au interface while for positive Au bias the current generation is near the GaAs interface.

The excitation in these cases probably arises in depletion regions at the interfaces. Applying a bias increases the field in one such region while decreasing it in the other. Furthermore, since the depletion region is widened, the interference effects should wash out at higher values of bias, as observed, because such effects can only be observed when the region of high field is substantially smaller than the optical wavelength in the film.

D. Double-Layer Oxide by Plasma Anodization

Composite insulating films consisting of a layer of native oxide (Ga-As-O) and aluminum oxide (Al_2O_3) were grown on GaAs by plasma anodization in a dc oxygen discharge. The layers were formed by evaporating a thin layer of metallic Al onto a clean GaAs substrate, followed by anodization in an oxygen plasma. During anodization the Al was first converted to Al_2O_3, then the GaAs was oxidized to produce a Ga-As-O layer sandwiched between the Al_2O_3 layer and the GaAs substrate. Depending on the plasma conditions, substantial intermixing of the oxide layers could occur and Ga and As were found to easily penetrate the Al_2O_3 layer. The electrical properties of the composite dielectric film were somewhat improved over the Ga-As-O film alone, but the electrical properties of the insulator/GaAs interface were very similar to those of samples without the Al_2O_3. Also, considerable excess As was found at the GaAs interface in the Al_2O_3/Ga-As-O/GaAs system, in marked contradiction to previously reported results for similar composite films found by a plasma-beam technique.

E. Silicon-Nitride Films

The electrical properties of Si-N films, formed by rf plasma deposition on GaAs, were measured. The films were deposited on both p- and n-type GaAs substrates at a temperature of 325°C using SiH_4 and N_2. Capacitive-voltage (C-V) and current-voltage measurements of MIS diodes were made to determine the bulk film properties and to characterize the insulator/GaAs interface. Auger electron spectroscopy was used to determine the Si/N ratio and to detect any contamination present. Results of the electrical measurements for the plasma Si-N films were compared to the properties of Si-N films formed by conventional, high-temperature chemical vapor deposition on GaAs and to films formed by anodization of GaAs. The bulk properties of the plasma Si-N films were found to be superior to the anodic oxides, but slightly inferior to the pyrolytic Si-N films. The plasma films exhibited a breakdown field of 4.5×10^{6} V/cm, a resistivity of $3\times10^{15}\Omega$-cm, a relative dielectric constant of 7.9, and an index of refraction, measured by ellipsometry, of 1.99. The composition of the plasma Si-N films were found to be very similar to the pyrolytic Si-N films, but with slightly lower oxygen contamination. The electrical properties of the plasma Si-N/GaAs interface, as indicated by the frequency dispersion of the C-V characteristics, differed from that measured for the oxide/GaAs and pyrolytic Si-N/GaAs structures. On p-type substrates, the plasma Si-N films showed very high interface state densities across the entire bandgap, unlike the anodic films. On n-type substrates, a preliminary analysis, based on 100 MHz C-V data, indicates that the minimum interface state density of the plasma Si-N/GaAs system is approximately 3×10^{12}cm^{-2}-eV^{-1}, similar to that characteristic of the anodic oxide and the pyrolytic Si-N. All three types of films exhibited significant majority carrier trapping and fixed charge at zero bias.

III. Publications, Presentations, and Theses

The following is a list of papers describing research funded by ONR:

1. L. A. Chesler and G. Y. Robinson, "DC Plasma Anodization of GaAs", Applied Phys. Letts 32, 60, (1 January 1978).

2. L. A. Chesler and G. Y. Robinson, "Plasma Anodization of GaAs in DC Discharge", J. Vac. Sci. Technol. 15, 1525 (July/Aug. 1978); presented at the Conference on the Physics of Compound Semiconductor Interfaces, USC, Jan. 1978.

3. T. R. Ohnstein, "Chemical Vapor Deposition of Silicon Nitride Films on Gallium Arsenide", M.S. Thesis, University of Minnesota, December 1977.

4. L. A. Chesler, "Plasma Anodization of Gallium Arsenide", M.S. Thesis, University of Minnesota, August 1978.

5. N. Hendrickson, "Plasma Anodization of Gallium Arsenide", M.S. Thesis, University of Minnesota, December 1978.

6. G. Y. Robinson, "Auger Analysis of Anodic Oxide and CVD Nitride Films on Gallium Arsenide", presented at the International Conference on Solid Films and Surfaces, Tokyo, Japan, July 1978.

7. T. R. Ohnstein, G. Y. Robinson, M. J. Helix, B. G. Streetman, and K. V. Vaidyanathan, "Electrical Properties of Plasma-Deposited Si-N Films on GaAs", paper WP-A4, presented at the Device Research Conference, Boulder, CO, June 1979.

8. N. K. Pu, "Al_2O_3/Ga-As-O Growth by Plasma Anodization", M.S. Thesis, University of Minnesota, 1980.

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