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FINAL REPORT

INVESTIGATION OF NOVEL TUNNELING PHENOMENA IN SEMICONDUCTORS

Leo Esaki

March 15, 1977

#### **U. S. ARMY RESEARCH OFFICE**

Contract DAAG29-76-C-0032

IBM Thomas J.Watson Research Center P.O.Box 218 Yorktown Heights, New York 10598

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) 20. cont'd. magneto-oscillations. Also, during the course of this study, the molecular beam epitaxy technique has been established to produce atomically smooth and coherent layers, and surface studies have been carried out to yield important information about surface reconstruction, surface states and oxygen adsorption characteristics. Law ". T. Warson Rea. Center . J. Marson Rea. Center . J. Has its, Forktown Raights, W.Y.10596 TEL EL doran water that the first of Baldisselond. Approved for public releases and the set appropriate the stand sensitive of the approximate from the second to many the president. Seriedic Samiconfrees Statuture Case Galla Esperiativel Gunnu Statige and Sub-bander Resonant Summailes and transport Teor Dimensional Sama and Resonant Annon Scatteing: Teor Dimensional Sand and Shohnikov-dednae Oscillation: Moleculer Reso Spitzary: Sand and Shohnikov-dednae Oscillation: Moleculer Reso Spitzary: Quastran states are drasted in peniformidden superioritess ande di periorite ditrathis invers of Gate and Gatha providing character beam spicary. Sy controlling the periodic periodic protecter, these states are controlled in searcy positions, bandmarking and an autocopy, whi shales an encent spical and alcotrolic transport protecties, a descreterations from a variaty of physical massurements such as tomorant formations photoconcurrity, resonant fuman sectorizes a SECURITY CLASSIFICATION OF THIS PAGE

## I. Statement of Objective

The project was undertaken to pursue studies of electron tunneling in monocrystalline semiconductors. Of specific interest are structures in which the potential profile in one dimension is controlled by the alloy composition of a compound semiconductor during epitaxial deposition. The profile varies in sophistication from the simple case of a single potential well to that consisting of periodic potential wells and barriers, known as a superlattice. Under the condition of an extremely thin well width, quantum states are created and become dominant in governing the transport and optical properties of the structures. The purpose of this project is to investigate this fundamental quantum mechanical phenomenon, the underlying physics, and ensuing electronic characteristics.

## II. Summary of Achievement

It was recognized that the success of this project hinged critically on our ability to produce extremely smooth and precisely controlled epitaxial semiconductor layers of high quality. The materials chosen were GaAs and  $Ga_{1-x}Al_xAs$ , which were deposited by the technique of molecular beam epitaxy (MBE) under the control of a digital computing system. The considerable experience, which we gained in the development of this technique through the partial sponsorship of a previous ARO Contract (DAHCO4-72-C-0025), was in a large measure contributing to the various achievements in the present project. We have not only observed resonant tunneling or, more generally, resonant transport, and thereby established the energy positions of the quantum states;

but also gained knowledge and insight of the band structure of these states themselves to correlate their width and dimensionality with the observed optical and conduction properties. These are the major points to be described in the following. In addition, we will also summarize briefly the results in the areas of growth and evaluation, and of surface studies, which were initiated to help assessing and improving the layered structures but were broadened in scope subsequently for their own interest.

# (A) Growth and Evaluation

The MBE system was modified to completion by incorporating a large reservoir of metallic As source and a substrate holder capable of mounting multiple substrates. This combination made it possible to perform several depositions without breaking the ultrahigh vacuum condition, and a large number of runs without recharging the source. The extra degree of cleanness achieved in this fashion was translated into a superior quality of the epitaxial films in terms of carrier mobilities and luminescent intensities. Also incorporated into the system was an Ar- bombardment facility, its routine application for substrate cleaning prior to deposition resulting in consistently smooth and featureless film finish.

The periodic structures grown by the MBE were evaluated by x-ray techniques, using both small- and large-angle reflections. In the former case, interference peaks of different orders were observed in agreement with those calculated theoretically both in angular positions, intensities and linewidths, indicating a degree of interfacial smoothness and periodic coherency on the

scale of atomic dimensions. A detailed analysis of the results from the largeangle reflections, in addition, indicates that the periodic structure is approximately commensurate, i.e., it comprises an integral number of atomic layers of GaAs and AlAs (or GaAlAs) with the latter being strained, without relaxation by dislocations, to conform with the lattice parameter of the substrate GaAs along the plane of the layers. The x-ray technique is by far the most powerful in establishing metallurgically the periodicity of the superlattice.

The composition-depth profiling technique by a combination of ionsputtering and Auger-spectroscopy, used earlier to resolve the periodic layers, was extended to study the interdiffusion rates between GaAs and AlAs. By examining the profiles of Al and Ga in sandwich structures after annealing, diffusion rates were established both as a function of temperature and as that of Al-composition. Values as low as  $10^{-18}$ cm<sup>2</sup>/sec, for the first time, could be investigated by this technique. The results not only confirm the negligible diffusion effect at the growth temperature of the superlattice structures but also provide the much needed, quantitative information about these technologically important semiconductors.

#### (B) Electronic Properties

The first clear evidence of the existence of the quantum states was obtained from tunneling measurements in double-barrier structures in which a single well is sandwiched between two barriers. Impinging electrons with energies coinciding with the quantum states in the well are able to transmit through the barriers with ease, known as resonant tunneling; while electrons with other energies are severely attenuated. The current-voltage characteristics, then, show a series of peaks which can be correlated to the quantum states. This kind of behavior was observed and found in good agreement with theoretical predictions in a large number of samples, where we have varied the thickness of the well and, consequently, the energy positions of the quantum states. The phenomenon of resonant tunneling has long been predicted theoretically as one of the most fundamental consequences of quantum mechanics. But it has hitherto eluded experimental verification because of the stringent requirements.

The involvement of the quantum states in tunneling was also manifested in the transport measurement in a tight-binding superlattice, i.e., one with a relatively strong periodic potential. At applied voltages beyond which the band conduction cannot be maintained in the structure, the current is limited by electron tunneling through a barrier between the ground state in one well and the second quantum state in a neighboring well. This proceeds in the superlattice from one region to another, resulting in a current or conductance oscillation as a function of voltage. The observed period of such oscillation agrees with the calculated energy difference between the ground and the second states.

Direct determination of the energy positions of the quantum states, as opposed to those deduced from transport properties, came from optical experiments, including absorption, reflectivity, and luminescence measurements. In this situation, both the states for electrons in the conduction band and those for holes in the valence band are involved. In the photoluminescence measurements, the emitted photon energies correspond to interband transitions between

the ground states, while both these transitions and those involving the second and higher states manifest themselves as well-defined peaks at the excited photon energies in the absorption spectra.

The interrelationship between the quantum states and the ensuing transport properties in a superlattice was demonstrated in photoconductivity measurements, in which both the photon energy of excitation and the applied voltage were varied independently. The spectral response at a fixed voltage identifies the various quantum states in a similar manner as in absorption measurements, with the advantage of correlating the intensity with the width of the states which is a measure of the ease of band conduction. On the other hand, the photocurrent as a function of voltage, at a given photon energy corresponding to transitions between the states, shows a pronounced negativeresistance characteristic which was predicted theoretically and observed experimentally from previous d.c. transport measurements.

Having largely established the energies of the quantum states and the role they play in governing electron flow, attention was recently directed to the states themselves or, more specifically, to their characters of anisotropy and dimensionality. As the strength of the periodic potential increases, the quantum states narrow in width and eventually become discrete levels with energyindependent density-of-states of two dimensionality. Resonant Raman experiments were performed, where the scattering intensity is related to the densityof-states, and strong enhancement of the resonance was observed. The resonance occurs at energies corresponding to the interband transitions between the

states and with intensities decreasing as such states become less twodimensional in nature. A theory was developed to give a quantitative fit to the resonant curves obtained from different superlattice samples with different degrees of two dimensionality.

The conduction properties along the layers of the superlattice under a magnetic field were investigated. Magnetic quantization was observed, the magneto-resistance exhibiting Shubnikov-de Haas oscillations with respect to the field. The period of oscillation depends on the cosine of the angle between the field orientation and the current flow for two-dimensional states, but becomes independent of the orientation for the three-dimensional states. By varying both the periodic potential and the electron concentration, superlattices with a wide range of quantum states have been examined, including these two extreme cases as well as those with intermediate dimensionalities and multiple states. The results were well interpreted from the calculated Fermi energies and density-of-states. This work, together with the resonant Raman work, exemplifies a classic situation in research: The measurements lead to valuable information about the quantum states in a superlattice, while the superlattice in the meantime provides a unique medium with intriguing electronic configurations to pursue and to understand the various processes on which the measurements were based.

(C) Surface Studies

The success of the MBE technique in growing high quality and atomically smooth layers suggested that the technique could be applied readily to the generation and subsequent study of clean, well characterized surfaces. Previous methods of preparing clean surfaces of compound semiconductors were restricted to cleavage surfaces, while ion-bombarded and annealed surfaces were generally deficient in the more volatile chemical constituent, such as As in GaAs.

Much of our efforts were concentrated on the (100) surface of GaAs, which consists of alternating layers of Ga and As atoms. With MBE it is possible to terminate the (100) surface with either the Ga or As atoms, as well as with a variable combination of both. In the case of an equal amount of both atomic species, the surface becomes essentially nonpolar. Such a surface is characterized by its own rearrangement of surface atoms or surface reconstructions. Other surface reconstructions are also observed on this plane with only one atomic species being present, as well as on other crystallographic planes. Such atomic rearrangements are studied by high energy electron diffraction.

A somewhat simplified view of the surface consists of a plan of atoms with one or more severed bonds. If these atoms are arsenic, with inherently 5 valence electrons, it is expected that the severed bonds (frequently referred to as "dangling bonds") are filled. On the other hand, if the surface atoms are gallium (with only three valence electrons which are involved in the bonds to the second-layer As atoms) it is expected that the dangling bonds be empty. Although such a picture had been proposed on theoretical grounds it was not experimentally verified until recently.

By using the analytical technique of electron energy loss spectroscopy, which may be thought of as an analog of optical spectroscopy, we have verified the existence of both empty Ga-derived and filled As-derived surface states. The technique consisted of exciting 3-d core electrons into empty surface states of the Ga-exposed surface and observe their disappearance as the surface was progressively covered with As. The filled surface states were deduced from features in the energy loss spectrum associated with excitations from such states into the empty surface states. An important conclusion from these studies was that the surface states are highly localized in the surface region and little overlap exists between them and the bulk states. These studies were extended to the other principal planes of GaAs, as well as to MBE grown AlAs, ZnSe and Ge.

The electron energy loss spectroscopy was extended to include losses arising from excitations from deep core levels. Because of their localization as well as definite orbital symmetry, it is possible to determine the origin and symmetry of the final, empty valence states. Using such core exitations we have demonstrated the existence of empty-dangling bond surface states in Si, as well as elucidated the conduction band structure of SiO<sub>2</sub>.

Our studies were further extended to include the oxygen desorption characteristics of a variety of semiconductors. For instance, it was determined that oxygen adsorbs atomically on both Ge and Si, with an oxygen atom double bonded to a single surface atom. The oxygen adsorption also seems to be dissociative on the GaAs surface, and we demonstrated that contrary to previ-

ous proposals, the Ga atoms are included in the oxidation process on the nonpolar surfaces. One of the more interesting adsorption characteristics is exhibited by the ZnSe(100) surface. This surface is inert to oxygen adsorption up to oxygen pressures of about 0.01 mm of Hg. A sudden, irreversible uptake of oxygen occurs above this pressure with the formation of a relatively inert oxide.

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- **IV.** Participating Personnel

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