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ON THE ARTIFICIAL SEMICONDUCTOR MATERIALS

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ABSTRACT

For about the last three decades, semiconductor technology began to make its most apparent impact in Solid State Electronics. The field of photonics, which combines laser physics, electro-optics and nonlinear optics has expanded tremendously. Notably, modern light wave communications exemplify photonic systems. Here, optical signals are generated, modulated, transmitted, and detected before they are transformed to electrical form for final use. Optical processing of information has notably been found to possess several advantages over electronic processing, which must usually be done serially and is limited in speed by the broadening of pulses in interconnecting wires and also limited in density by cross talk between those wires. Optical systems capable of handling very large quantities of data is now awaiting only the development of convenient digital optical logic elements with low switching energy. An ideal material for opto-electronic applications as mentioned above should be able to transform light into current and vice-versa for emission and detection. The material should also exhibit large electronic and optical nonlinearities that would allow one to use it as a transistor and optical gate. These materials which are currently internationally studied are presented in this paper.

INTRODUCTION

Heteroepitaxy is of fundamental interest for the growth of Superlattices (SL) and Multiple Quantum Wells (MQW) systems. Steady improvements in growth techniques such as Molecular Bean Epitaxy (MBE) *(Cho 1971; Cheng et al 1981; Gossard 1982, 1986)* and Metal Organic Chemical Vapour Deposition (MOCVD) *(Dupius et al 1978, 1979, Razeghi and Duchemin 1984)* about the last three decades have made possible the production of high quality heterostructures (SL and MQW) having designed potential profiles and impurity distributions with dimensional control close to inter atomic spacing and with virtually defect free interfaces, particularly in lattice matched cases such as GaAs/AlGaAs and GaInAs/AlInAs systems. In addition to MBE and MOCVD, there are other techniques such as gas source (GS) MBE *(Panish and Sumshii 1984)*, low pressure (LP) MOCVD *(Raseghi and Duchemine 1984)*, Chemical Beam Epitaxy (CBE) *(Tsang 1984)*, Hot Wall Epitaxy (HWE) *(Fujiyasu et al 1984)* and Atomic Layer Epitaxy (ALE) *(Pessa and Jylha 1984)* which have been explored for this purposer.

The III-V semiconductor compounds which are made from groups III and V elements have the basic properties necessary for fabricating SL and MQW. These semiconductors have direct band gap. Thus they can emit or absorb photon or light energy and consequently are very efficient absorbers and emitters. They also have large carrier mobilities and are easily doped. More importantly, they can form various solid solutions with identical crystal structures and well-matched lattice parameters but with different energy gaps and refractive indices. The chemical and physical compatibilities of solid solutions of the various III-V compounds make it possible to grow heterostructures which are

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generally known as low dimensional structures (LDS) *(Adelabu 1996a)*. The semiconductor SL and MQW structures have been grown with not only III-V compounds but also with II-VI and IV-VI compounds and also with elemental semiconductors as well as amorphous materials.

Heterostructures or LDS grown with pairs selected from the above grouped materials apart from those mentioned also include InP lattice matched alloys *(Cheng et al 1981, Razeghi and Duchemin 1983, Voos 1983)*. The introduction of II-VI compounds apparently extended the available range of energy gaps in both the high and low directions. That of ZnS is as high as 3.8eV while all the Hg compounds have a negative energy gap or can be called zero gap semiconductors. The magnetic compounds CdMnTe *(Bicknell et al 1984, KolodziejSki et al 1984)* are newcomers in the SL and MQW arena. In the rest of the paper are discussed:

iv. The developmental path in the research of the LDS;
v. The physics and structure of the material, and
vi. Some of the novel characteristics of the materials.

Brief History

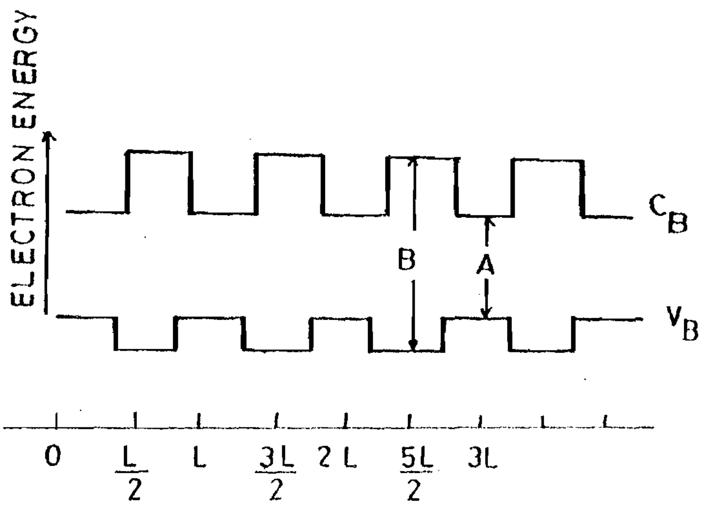
The developmental path in the research of semiconductor SL and MQW in the past thirty years have left a significant milestone. Research on these materials was initiated through a proposal by *Esaki and Tsu (1969, 1970)* for a one-dimensional potential structure engineered with epitaxy of alternating ultrathin layers. In anticipation of advancement in technology, two types of SL and MQW were envisioned-compositional *(Dingle et al 1974)* and doping *(Dohler 1972a, b)* structures figs 1a and b. The idea of SL occurred to *Esaki and Tsu (1969, 1970)*, while examining the feasibility of structural formation by epitaxy for potential barriers and wells thin enough to exhibit resonant electron tunnelling *(Bohm 1951)* through them. Such resonant tunnelling arises from the interaction of electron waves with potential barriers. *Esaki and Tsu (1969, 1970)* attempted the formidable task of engineering such quantum structures which warranted serious effort. The effort of these pioneer workers *(Esaki and Tsu 1969, 1970)* was indeed to search for novel phenomena in quantum regime with precisely engineered structures. In their effort, they showed theoretically that, SL and MQW considered a natural extension of double and multiple-barrier structures possess unusual electronic properties of quasi-two-dimensional character. Unfortunately, their early effort failed because of serious technological problems. In 1972, another effort by them *(Esaki et al 1972)* proved successful. They found that Molecular Beam Epitaxy (MBE) grown GaAs-AlGaAs SL exhibited a negative resistance in its transport properties, which was, for the first time, interpreted in terms of SL effect. Though the early efforts focussed on transport measurements, *Tsu and Esaki (1971)* calculated nonlinear response of the conduction, electrons in a SL medium, leading to optical non-linearity *(Gribnikov et al 1995)*.

PHYSICS AND STRUCTURES OF THE MATERIALS

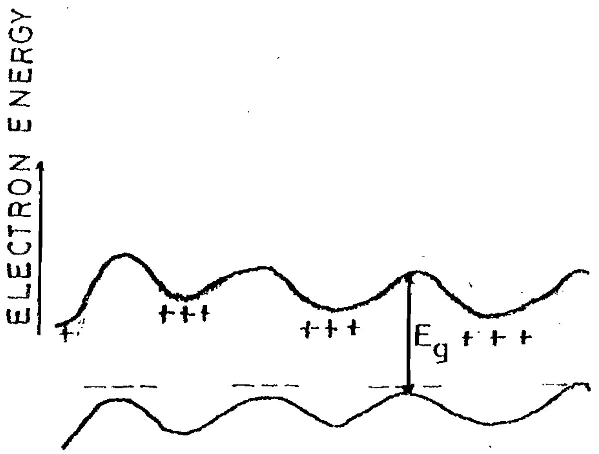
Usually, electrons and holes can propagate freely in the periodic potential of semiconductors. Two major changes in the dynamics of these charge carriers caused by the semiconductor environment are:

i. The replacement of the free carriers (electron and hole) masses by much smaller effective masses.
ii. A substantial increase in the dielectric constant.

As a consequence of these changes, basic physical quantities such as the Bohr radius ranges from 10Å to 500 Å. This corresponds to effective Rydberg constants ranging from 1meV to 100meV *(Adelabu 1996a)*. The change of scale in natural units causes a number of



(a) TYPE 1 COMPOSITIONAL

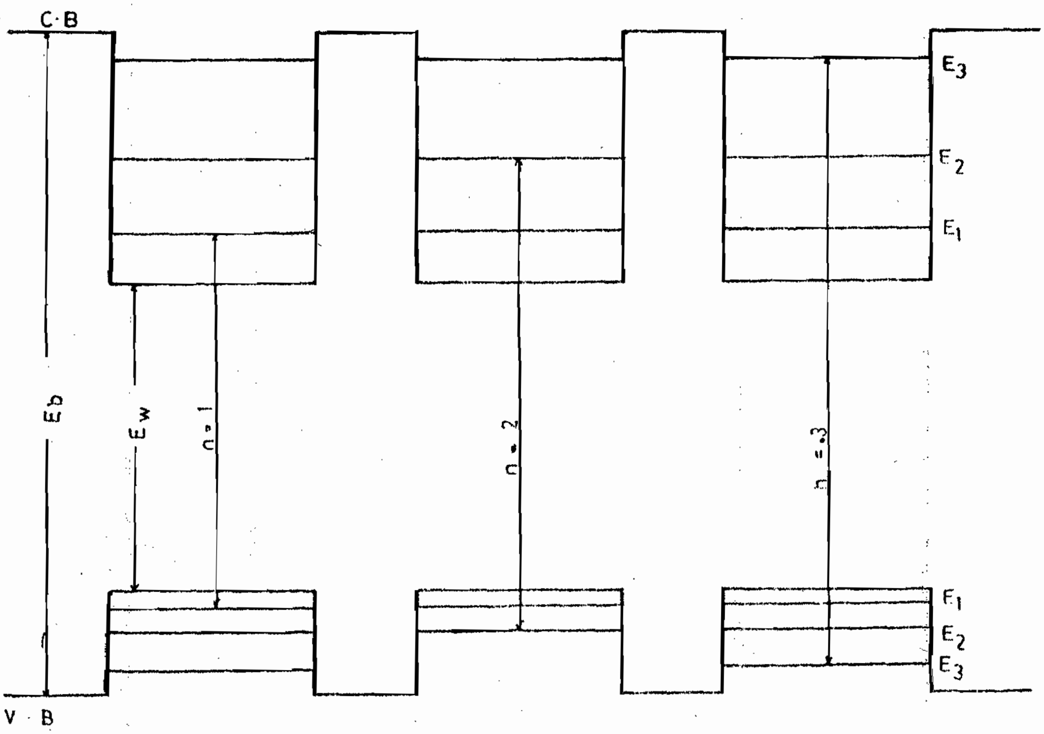


(b) DOPING
SL — MQW

FIG-1

processes involving electrons and holes in semiconductors to be different from the free space atomic processes that they parallel. Carriers (electrons, holes, excitons) in semiconductors are more sensitive to small perturbations. This is a situation that one can exploit for device applications and one that can be used to obtain model systems not ever encountered with free particles. In low dimensional structures *(Adelabu 1996a)* modifications of free-particle behaviours due to quantum size effects (QSE) are important. QSE arise when the dimensions of a quantum system become comparable to the Bohr radius. These effects can be observed in semiconductor microstructures that have dimensions of the order of 100Å. The simplest examples of systems where size produces fundamental modifications of optical and electronic properties are quantum well structures. These structures consist of ultrathin layers of two or more compounds grown one on another periodically *(Dingle et al 1974)*. Because the layers have different band gaps, the energy bands present discontinuities in real space (fig. 2). Quantization of the carrier motion in the direction perpendicular to the layers produces a set of discrete energy levels. If the energy discontinuities are large enough and the layers with the larger band gaps (i.e. the barriers) are wide enough, then there will be little interaction between adjacent low-gap regions. The carriers confined in each of those layers will behave almost independently, and thus, the name-quantum well structures. When the barriers are narrow, or when the energy of a state is comparable to the energy discontinuities, the interaction between layers is important. The wave functions of the carriers are extended perpendicularly to the layers so that the behaviour of the carriers is modified by the periodic long-range modulation superimposed upon the crystalline potential. Hence, the name superlattices *(Adelabu 1996a)*.

In quantum well structures electrons and holes do not move with their usual three degrees of freedom. They show one-dimensional (ID) behaviour normal to the layers. This reduced dimensionality induces drastic changes in the electric and optical properties of these man-made semiconductor materials.



FIG·2

One advantage of these materials is that impurities can be introduced into the larger gap material (i.e. the barrier layer) in such a way that the impurity nuclei will be trapped while the carriers that are introduced can migrate towards the low-gap layers (i.e. the wells) and form a 2D-gas at the interface. This aspect is known as modulation doping. *(Dingle et al 1974, Stormer et al 1981, Stormer 1984, Hasbun 1995)* fig. 3. Modulation doping produces a physical separation between impurities and carriers and consequently leave the carriers highly mobile. Solid state physicists have taken advantage of this particular property in the fabrication of some devices and in the fundamental studies in integral and fractional quantum hall effects *(Wei et al 1984)*. In the LDS, the conduction and valence bands become sets of 2D-subbands with step-like density of states fig. 4. This increases the number of states that contribute to the optical transitions of the absorption edge. Device designers have used this effect to obtain very-low-threshold diode laser and others by including quantum wells in the active region of the diode and other devices *(Smowton and Blood 1995, Kane et al 1995, Guo et al 1995)*.

NOVEL CHARACTERISTICS OF SL AND MQW

A particle of importance in LDS is the exciton. When a high-purity bulk semiconductor absorbs a photon, the electron that is promoted to the conduction band interacts with the hole left in the valence band. The electron and hole thus form a bound state analog of the hydrogen atom called an exciton. This final state interaction produces a set of discrete and very strong absorption structures just under the band gap fig. 5. Because the binding energy of the exciton (i.e., the energy of the first state or its effective Rydberg constant) is very small exciton are very fragile. They are noted to be very sensitive to any kind of defect and in bulk materials are usually observed only at low temperatures since they are easily broken apart by thermal phonon. However, in a quantum well system with layer thicknesses smaller than the Bohr radius, the exciton modifies its structure to fit into the low-gap layers (i.e. the wells). It flattens and shrinks. The electron and the hole are forced to orbit closer to each other with the binding energy increasing by a factor of two or three. This added stability makes the exciton's resonances observable at room temperature as is clearly demonstrated in the absorption spectrum fig. 5. Usually, one can observe steps assosicated with the transitions between subbands and the exciton peaks before the steps. As earlier stated, in the case of ultrahigh purity bulk semiconductor, exciton peaks clearly resolved as in the case of quantum wells are only observed at very low temperature. The peaks are so apparent in quantum well structures for two reasons:

i. The increased exciton binding energy.

ii. The confinement strongly enhances the contrast with the continuum.

Contrary to what exists in the bulk GaAs where only one exciton resonance is observed, the reduced symmetry of quantum well structures produces two valence bands and hence two excitons which result in the double peak seen at the onset of the first transition and are associated with the electron to heavy hole transition and electron to light hole transition fig. 6.

Optical effects associated with excitons have the been found to play a crucial role, in many opto-electronic applications of quantum well structures. For undoped quantum well structures, excitonic effects are further modified by the confinement of carriers. When a source of light tuned to the exciton peak illuminates a quantum well structure, bound electron-hole pairs are first generated and then quickly ionized by the large population of thermal phonons present at room temperature where the average thermal energy KT is about three times larger than the exciton binding energy. Excitons in

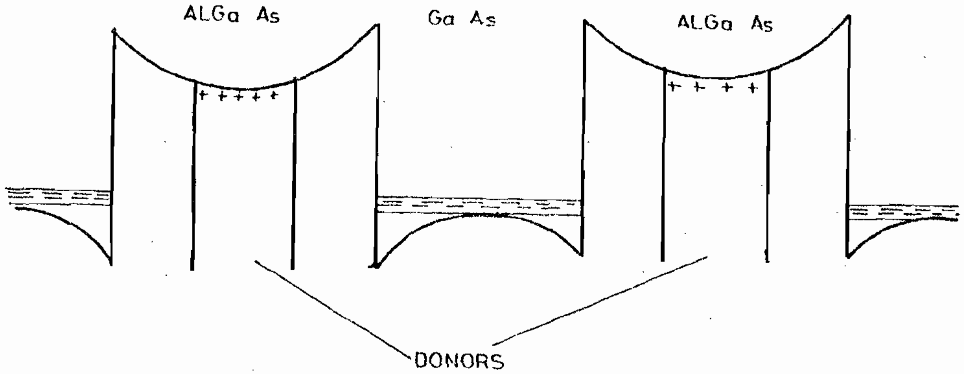
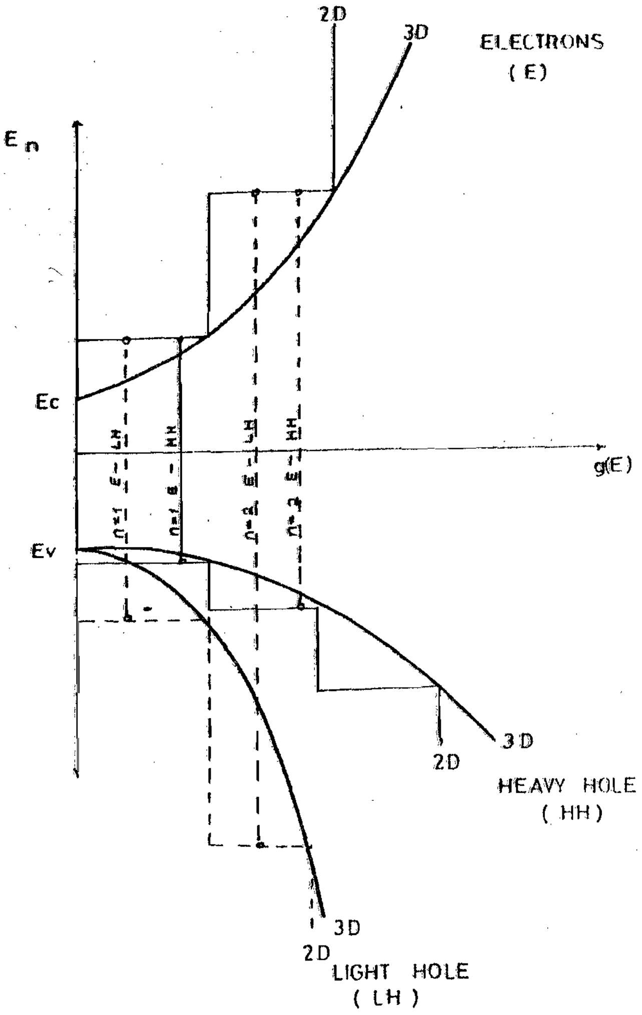


FIG.3



FIG·4

quantum wells are also sensitive to electrostatic perturbations. Because the carrier wave functions extend to about 100Å, and because the confinement or binding energies are only 10-100 meV, moderate electric fields of the order of 10 meV per 100Å or 10^4 V/cm cause significant perturbations. When an electrostatic field is applied to a 3-D exciton, it induces a stark effect analogous to that seen in atoms *(Kim et al 1995)*. There is a small shift in energy levels that is quickly masked because the energy levels are broadened by the excitons ionized under the influence of the electric field. This can be seen in quantum well systems when the field is applied paralled to the plane of the layers. With a perpendicular field, an absolutely new process occurs. The field pushes the electron and hole apart. However, the walls of the well prevent ionization by constraining the particles to stay close enough to remain bound. Ionization can only occur when the particles tunnel out of the well. Consequently, it is possible to apply fields as large as 50 (fifty) times the classical ionization field including redshifts in the absorption peak which is 2.5 times the binding energy and still observe exciton resonances. This phenomenon is called the quantum confined stark effect *(Kim et al 1995, Chemla et al 1983, Lozovik and Ovchinnikov 2001)*. The observed shifts due to this effect are well accounted for by the field induced variations in the energy of the single particle state and by pair attraction *(Miller et al 1984)*. This effect also allows one to shift an abrupt and highly absorbing edge into a spectral region where the sample is normally transparent. Such shifts have obvious applications in optical modulation and optical logic.

In quantum wells, the conduction band and the valence band do not contribute equally to the total band gap discontinuity at a heterojunction. Measurements of these parameters indicate that the change in the energy level of the bottom of the conduction band, as one crosses a heterojunction is about 1.5 times the change in the energy level of the top of the valence band across the junction *(Dingle et al 1974)*. This intrinsic asymmetry between electrons and holes can produce specular effects such as impact ionization, which depends critically on energy gains at the heterojunctions. New types of photodectors take advantage of this asymmetry. In low temperature measurements on MQW structures, several exciton peaks associated with different bound electrons and bound hole states have been observed *(Dingle et al 1974, 1975)* well

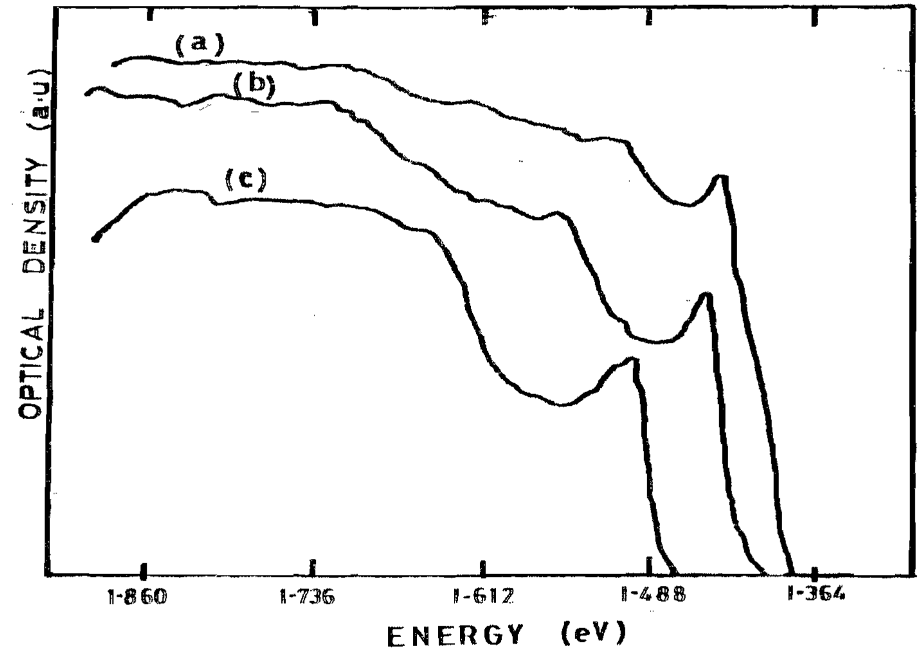


FIG. 5

resolved. The spectra at low temperature also clearly indicate the evolution of resonantly split, discrete states into the lowest subband of a SL. From the analysis of such spectra, the electron and hole well depths were determined to be 85% and 15% of the total energy gap difference respectively *(Dingle et al 1974)*. However, these values have been revised to about 67% and 33% for the GaAs/AlGaAs systems after a prolonged controversy *(Adelabu 1993, 1998)*

Photocurrent measurements on the GaAs/AlGaAs SLs subjected to an electric field perpendicular to the well plane via a semi-transparent Schottky contact have been made *(Tsu et al 1975)*. These experiments confirmed that a series of peaks in the photocurrent spectrum correspond to transitions between quantum states in the valence and conduction bands. The photocurrent voltage curve was observed *(Tsu et al 1975)* to exhibit a pronounced negative resistance when the energy difference between the adjacent wells exceeded the SL band width . In undoped high-quality GaAs-AlGaAs quantum wells grown either by MBE *(Miller et al 1980; Weisbuch et al 1980, 1981; Petroff et al 1981)* or by MOCVD *(Vojak et al 1980)*, the main photoluminescence (PL) peak was attributed to the excitonic transitions between 2D-electrons and holes. The field induced effect on the PL in such quantum wells was studied in 1982 *(Mendez et al 1982)*. This was the first time in PL measurements that the electric field was applied perpendicular to the well plane with the use of a Schottky barrier configuration. The spectra in the experiments revealed pronounced field-effects which indicate two peaks associated respectively, with exciton and impurity, related recombination. With increasing field, the peak position was observed to shift to lower energies, the intensity decreases, with the exciton structure decreasing at a much faster rate, and completely quenched

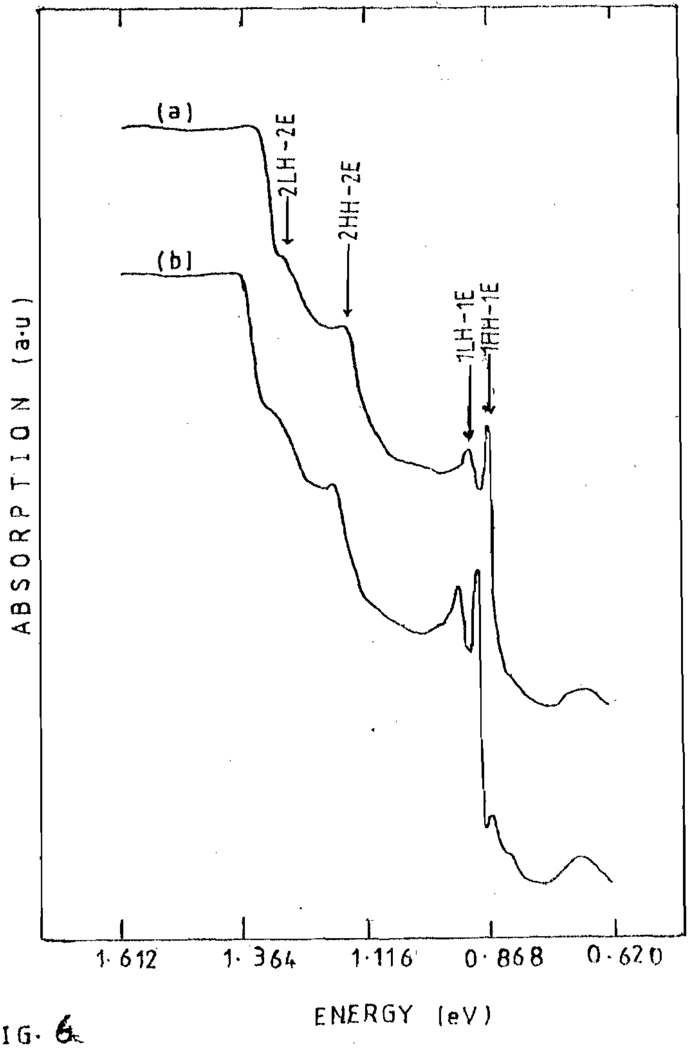


FIG. 6

at a field a few tens of kV/cm. These results were interpreted as being caused by induced separation of confined carriers and modification of the quantum states. *Chemla et al (1983)* observed a large shift of the excitonic absorption peak by applied electric field, even at room temperature. *Miller et al*, the coworkers of *Chemla (Miller et al 1984, 1985)* attempted to explain the phenomenon that the exciton resonances remain resolved for shifts much larger than the zero-field binding energy.

Usually, free carriers (electrons and holes) created in semiconductors by impurities inevitably suffer from impurity scattering, though with a few exceptions such as in Silicon metal-oxide-semiconductor field effect transistors (Si-MOSFET) where electrons or holes are induced by applied gate voltages and in InAs-GaSb heterostructures, where electrons and holes are produced solely by electron transfer. As earlier stated, SL and MQW have made it possible to spatially separate free carriers and their parent impurity atoms by doping impurities in the region of the potential hills (i.e., modulation doping fig.3). Though this concept was expressed in the original article by *Esaki and Tsu (1970)*, it was only *Dingle et al (1978)* who successfully implemented such a concept in modulation-doped GaAs-AlGaAs SLs, achieving electron mobilities far exceeding the Brooks-Herring prediction. Modulation doping was performed by synchronizing the Silicon (n-dopant) and aluminium fluxes in the MBE, so that the dopant was distributed only in the GaAlAs layers and was absent from the GaAs layers. Soon after *Stormer et al (1979)* reported a high-mobility 2D-electron gas in modulation doped GaAs-GaAlAs heterostructures. These heterostructures were used to fabricate a new high-speed FET called modulation doped FET (MODFET) *(Mimura et al 1980, Delescluse et al 1981)*. The device, if operated at 77K, exhibited a performance three times faster than that of the conventional GaAs metal-semiconductor FET (MESFET). Hall mobilities in the dark at 4.2K for confined electrons in high quality heterostructures exceeded $10^6 cm^2/V.S$ where a low temperature persistent photoconductive effect was noticed. Such persistent photoconductivity was also reported in InGaAs-InP heterostructures *(Hieblum et al 1984, Mendez et al 1984, Liu et al 1984, Drummand et al 1982; Stormer et al 1981, Wei et al 1984)*. Of recent *(Topinka et al 2001)*, there has been the observation of coherent branched flow in a two-dimensional electron gas.

Other SLs like n-i-p-i structure have also been produced. The periodic n-i-p-i structure is an outgrowth of a doping SL in the original proposal by *Esaki and Tsu (1970)*. *Dohler (1970a,b) and Ploog et al (1981)* pursued the production of this structure. The periodic rise and fall of the band edges is caused by periodic variation of impurity doping. If this SL is illuminated, extra electrons and holes are attracted to a minimum in the conduction band and to a maximum in the valence band respectively. Thus, those extra carriers are spatially separated, resulting in anomalously long lifetimes. An interesting consequence of this fact is that the amplitude of the periodic potential is reduced by the extra carriers, leading to a crystal which has a variable energy gap. *Vojak et al (1986)* attributed photopumped laser emission at low energies to donor-to-acceptor transitions that occur after a GaAs doping SL is excited to a flat-band condition.

Readers are referred to some of the publications by *Adelabu (1993; 1995a,b,c; 1996a,b,c, 1998)* that by *Adelabu and Abdullahi (1997)* and those by *Adelabu et al (1988, 1989, 1997, 1998)* for information on specific aspects in the field.

CONCLUSION

The new degree of freedom offered in semiconductor research through advanced material engineering has inspired many ingenious experiments which resulted in observations of not only predicted effects but also totally unknown phenomena among which is fractional quantization which requires novel interpretation. Activities in the new frontier of semiconductor physics have given immensurable stimulus to device physicists and have led to unprecedented transport and optoelectric devices and is provoking new ideas for applications.

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