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A Review of Semiconductor Heterojunctions

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The article serves as an introduction to a comprehensive list of references on semiconductor heterojunctions. Several methods of producing such structures are given, together with a table of materials between which heterojunctions have been formed. The more important measurements which are made on semiconductor heterojunctions are discussed and typical results quoted. A brief description of band models proposed for various heterojunctions is given. The references are arranged by year and in alphabetical order for convenience. Several articles are included which are not referred to in the text: these articles are included since they discuss certain theoretical aspects and possible practical applications of semiconductor heterojunctions.

1. Introduction

A heterojunction is a junction between two, dissimilar, crystalline materials where the crystal structure is continuous across the interface. This type of structure was first envisaged by Preston [1]. Gubanov [2, 3, 5] produced an analysis of heterojunctions with n-n, p-p, and p-n combinations, and Shockley [4] proposed a circuit device incorporating a change in the magnitude of the forbidden gap in the transition region of a p-n junction. Kroemer [6, 7] proposed the use of a heterojunction as a wide-gap emitter to increase the injection efficiency of transistors.

The experimental investigation of heterojunctions became feasible with the advances in materials technology associated with the preparation and purification of semiconducting materials [8, 9]. Heterojunctions pose inherent difficulties in fabrication, since lattice mismatches over the boundary must be accommodated, as must differences in thermal expansion of the associated materials when the junctions are prepared at elevated temperatures. The experimentally observed properties of a heterojunction can be difficult to interpret when thermal effects strain the junction and where the continuity of the crystal structure and purity of the two materials at the interface is in some doubt.

This article reviews the methods of heterojunction preparation and also indicates some of the measurement techniques that have been used in the study of heterojunctions. Finally, the theoretical models are noted which may be used to explain the properties of heterojunctions.

2. The Preparation of Semiconductor Heterojunctions

2.1. Epitaxial Growth from the Vapour Phase

The development of epitaxial growth (RCA Review, December 1963) has been the greatest stimulant to research in heterojunctions. Basically, the technique involves introducing one of the semiconducting materials in the vapour phase to condense on a crystalline substrate. The substrate controls the orientation of the layer and the layer is termed epitaxial. The technique allows the layers to be doped to any particular level and with a high degree of precision. In many cases, epitaxial growth from the vapour phase may be obtained at relatively low temperatures in simple, open tube, or flow systems. This technique has been used widely for producing heterojunctions between elemental semiconductors and III-V compounds [10, 13, 40, etc].

2.2. Vacuum Evaporation*

The vacuum evaporation technique uses single-crystal substrates, and materials of desired

*Although, clearly, epitaxial growth can occur in these circumstances too, usage commonly differentiates pure vacuum evaporation processes from those involving chemical reaction or decomposition as in section 2.1.

purity may be evaporated onto these substrates at various temperatures. Film thickness and rate of deposition are easily controlled, but accurately controlled doping is difficult. The introduction of stainless-steel, ultra-high vacuum equipment should improve the purity of the deposited layers. Vacuum evaporation has been used to form heterojunctions between elemental semiconductors as well as between many other materials [43, 44, 68, 81, etc.].

2.3. Alloying Techniques

An alloyed heterojunction may be produced either by melting all the lower-melting-point material [32] or by melting only the interface between the two materials [47]. The electrical properties of heterojunctions, prepared by either of the above techniques, do not appear to be dependent on the method of preparation. Both of these methods are important because the fabrication techniques are simple.

2.4. Other Techniques

Heterojunctions have also been prepared by diffusion [9], recrystallisation [41], growth from the liquid state (e.g. travelling solvent method [51]), sintering [78], and growth from an aqueous solution of reacting chemicals [88].

Table I gives an index to the references for various heterojunction arrangements.

TABLE I Materials index.

Material	Material	Reference
1	2	
Al_2O_3	CdS	43
CdS	CdSe	68, 96
	CdTe	43
	Cu_2S	27
	Si	56
	SiC	82
	SiO_x	43
	ZnTe	15, 23
CdSe	Ge	76
	ZnSe	63
CdTe	GaAs	54
Cu_2S	ZnS	35
Cu_2Se	ZnSe	35
GaAs	$GaAs_xP_{1-x}$	79
	Ga_xIn_{1-x}	61
	GaP	9, 31, 51, 54, 55, 87
	GaSb	47, 80
	$GaSb_xAs_{1-x}$	61
	Ge	10, 11, 13, 16, 17, 19, 33, 37-39, 42, 46, 47, 49, 51- 53, 58, 75, 81, 86, 97, 100, 102, 104-106
	InP	29
	InSb	64
$GaAs_{1-x}P_x$	Ge	59
GaP	Ge	21, 50, 51, 83
GaSb	InAs	80
	InSb	41, 69
Ge	Si	32, 36, 40, 44, 57, 66, 67, 85, 89, 90, 95, 97, 98
	Sic	62, 107
	PbS	88
	ZnSe	84, 99
Si	Sic	62, 65
	SiO_2	71, 72
ZnSe	ZnTe	70
ZnS	CdS	110

3. Experimental Measurements and Results

There are several techniques which will confirm that a heterojunction has an ordered structure and that its properties are due only to the interface between the two semiconductors. If the junction has been prepared by vapour deposition or vacuum evaporation, then the layers can usually be made thick enough for back-reflection Laue X-ray photography; for very thin layers, electron diffraction techniques are required. For the thicker single crystals produced by alloying, little information is to be gained from standard X-ray measurements, and electron-beam techniques may be used to determine the interface structure [47]. Such methods are very useful in determining the position of changes in doping levels. Anderson [17] has used photovoltaic and thermoelectric probe methods to indicate that changes in the doping level occurred at the interface.

Once the heterojunction structure has been confirmed, more detailed information to clarify the band diagram may be found from the following measurements. In any electrical measurements, it is essential that the contacts to the materials be ohmic [29] if spurious rectifying processes are to be avoided.

3.1. Current-Voltage Characteristics

The standard current-voltage measurements enable the built-in junction potential to be found and thus yield information on the band structure

of the junction. It is usual to compare the characteristics with the diode equation

$$I = I_S[\exp(ev/\eta kT) - 1]$$

the symbols having the usual meaning. Departures from the ideal equation, for which η is equal to one, allow the behaviour of heterojunctions to be investigated in terms of the well understood processes involved in homojunctions.

Values of η around one suggest that interface states play little part in determining the characteristics of the junction. The lattice mismatch in Ge-GaAs heterojunctions is small and Anderson [10, 11, 17] has reported values of η of 1.1 for n-n, n-p, and p-p junctions. p-n heterojunctions in the above materials give characteristics which are resolved into three, straight-line sections at 78° K. As the bias is increased from zero, the values of η are 2.1, 16.7, and 8.3. The value 2.1 is indicative of generation-recombination and the value 8.3 is attributed to injected currents governing the characteristics. The value 16.7 is attributed to the voltage drop across the GaAs governing the current flow, and the conduction band was assumed to have a "notch" on the Ge side and a "spike" on the GaAs side. From measurements on n-n Ge-$GaAs_xP_{(1-x)}$ junctions, where the mismatch is a function of x, Chang [59] was able to show that mismatches of the order of 1% caused saturation effects in both directions. Similar effects have been reported in n-n Ge-Si heterojunctions by Oldham and Milnes [44], who suggest that the interface states cause depletion layers in both semiconductors. More normal characteristics were obtained by heavily doping either semiconductor causing the depletion region to be effectively restricted to one material. In this case, the direction of rectification depends upon which semiconductor is heavily doped.

Hampshire and Wright [40] have reported conventional characteristics with η equal to 1.56 for n-p^+ Ge-Si heterojunctions, which agree with Anderson's theory. There were experimentally only small, trapping, or recombination effects due to either surface states or states in the deposited germanium layer; the reason being that the epitaxially deposited layer had a low resistivity.

Values of η equal to 2 are indicative of a generation-recombination mechanism at the interface. This mechanism may be associated with materials like CdS which have many traps or with junctions complicated by the presence of semi-insulating layers in one of the semiconductors. Aven and Garwacki [23] have reported this effect in p-n ZnTe-CdS heterojunctions and have suggested a p ZnTe/semi-insulating CdS/n CdS structure. The double-injection phenomena associated with high trap densities was observed by artificially widening the semi-insulating layer. Measurements by Dale and Josh [61] on the alloy heterojunctions GaAs-$GaSb_xAs_{1-x}$, GeAs-$Ga_xIn_{1-x}As$, and GaAs-Mn_2As, indicated generation recombination at trapping centres or a p-intrinsic-n structure.

Double-injection phenomena have been reported in Cu_2S-CdS by Keating [27] and in SiC-CdS by Salkov [82]. At low, applied bias, Anderson's diffusion process is applicable, but at larger biases the bulk properties of CdS lead to double-injection currents. Heterojunctions of CdS with Al_2O_3, SiO_2, and CdTe have been studied by Muller and Zuleeg [43]. At −40° C, Schottky emission predominates but, at higher temperatures, the characteristics are of the form $I = kV^3$. This is due to space-charge-limited flow with trap filling such that the trap density varies exponentially with energy, or to space-charge-limited double injection of mobile carriers into the insulating region. The CdS-Al_2O_3 heterojunction displayed hysteresis effects as the temperature increased owing, it was thought, to the effect of interface states with small activation energy. Hysteresis effects in Ge-Si heterojunctions have been reported by Wei and Shewchun [32] using heavily doped heterojunctions subjected to alternating currents. Negative resistance effects were also noted.

Rediker *et al* [47] found that the direction of forward current for Ge/GaAs-interface, alloyed heterojunctions was always with Ge biased positively. This indicated that the rectification was probably governed by the impurity distribution at the recrystallised interface rather than the doping levels. The value of η was 1.2 and electron-beam microprobe analysis showed the structure to be bulk GaAs/thin layer Ge/thin layer GaAs/bulk Ge. Alloyed heterojunctions of GaAs-GaSb gave η equal to 0.9, indicative of a tunnelling mechanism. This tunnelling was thought to be due to a highly disordered interface structure, leading to a considerable reduction in the effective thickness of the barrier.

3.2. Junction Capacitance Measurements

Anderson [17] and Hampshire and Wright [40] have used a modified homojunction theory to predict a value of capacitance for a heterojunction, assuming that the doping of the semiconductor is constant up to the interface. If the heterojunction is not abrupt, the value of the built-in voltage obtained will disagree with the value from capacity voltage measurements. Oldham and Milnes [44] have given a detailed interpretation of capacity voltage characteristics for non-abrupt n-n heterojunctions. Longini and Feucht [74] have pointed out that no additional information about the interface may be obtained from these measurements. Further information about trapping levels may be obtained from detailed studies of capacity voltage characteristics when both frequency and temperature are varied. (M. J. Hampshire, Ph.D. Thesis, University of Birmingham, 1965.)

3.3. Optical Measurements

The more common measurements are with the radiation incident on the wide-gap semiconductor. Lopez and Anderson [42] have reported measurements on Ge-GaAs heterojunctions of all conduction types. In n-n, n-p, and p-p heterojunctions, the transition region is located in the material with the higher energy gap and with photon energies intermediate between the band gaps electron-hole pairs are created in Ge. The charge carriers cannot flow to the transition region, so photocurrents are only obtained with radiation of energies greater than the band gap of GaAs. In p-n heterojunctions, the transition region is located on the Ge side and a band-pass characteristic is observed, the wavelength of which is determined by the band gaps of the two materials. Similar characteristics have been reported by Alferov *et al* [34] and Rediker *et al* [47].

The influence of the radiation on the current voltage characteristic of a p-n Ge-GaAs junction has been reported by Agusta and Anderson [53]. This measurement confirms Anderson's suggestion that the conduction band had a "notch" on the Ge side and a "spike" on the GaAs side.

The n-n Ge-Si heterojunction has been investigated by Donnelly and Milnes [89]. For heterojunctions with heavily doped Si and radiation incident on Si, only generation of electron-hole pairs in the Ge leads to a photocurrent. This gives a band-pass characteristic consistent with the suggestion that for high Si-doping the depletion region is restricted to the Ge. In equally doped junctions, three modes of current generation are observed according to photon energy. Photons with energies greater than the Si band gap are absorbed in the Si, but because of the gradual absorption edge and long diffusion lengths of electrons in Si, a positive photocurrent results. For photons with energies intermediate between the band gaps, absorption takes place in the Ge, leading to a reversal of the photocurrent. The photocurrent becomes positive again for photons with energies less than the Ge band gap, this has been attributed to interface-state pumping.

Van Ruyven *et al* [83] have investigated the absorption in n-n Ge-GaP heterojunctions with radiation incident on and parallel to the junction. They show that the Fermi level at the interface is independent of the doping levels of the semiconductor, a strong indication that the interface is dominated by interface states.

3.4. Other Measurements

The effect of crystal orientation at the interface has been studied for n-n heterojunctions in Ge-GaAs by Fang and Howard [39]. Measurements of the barrier voltage indicated variation in conduction-band discontinuities with crystal orientation.

Esaki *et al* [37, 38] and Chang [58] have measured the interface conductance and surface mobility as a function of field in Ge-GaAs heterojunctions. The results show that interface states have densities less than $5.10^{10}/cm^2$ and this supports Anderson's assumption of negligible interface states. Acceptor-type interface states with densities of $5.10^{11}/cm^2$ were induced by prolonged heat treatment.

Kanda *et al* [67] have reported the effect of uniaxial stress on Ge-Si alloyed heterojunctions.

Pulse measurements on heterojunctions indicate that there is no charge storage and switching times of the order of 1 nsec are typical [17, 39, 44, 57]. In the case of n-n and p-p junctions, Anderson [17] attributes this to current flow by majority carriers only. For p-n and n-p heterojunctions, minority-carrier storage exists, but discontinuities at the interface prevent their return. Oldham and Milnes [44], Rediker *et al* [47], and Longini *et al* [74] have suggested that the extremely short switching times of p-n heterojunctions may be attributed to the presence

of very short-lived interface states at the junction, which act as recombination centres.

4. Heterojunction Models

4.1. Anderson's Theory

The advent of improved vapour-growth techniques for GaAs (R. P. Ruth, J. C. Marinace, and W. C. Dunlop, *J. Appl. Phys.* **31** (1960) 995) gave Anderson the first real opportunity to explain the experimental characteristics of Ge-GaAs heterojunctions. He put forward a simple model based on the electron-affinity differences of the two semiconductors and involving discontinuities in the conduction and valence bands at the interface [10, 11, 17]. The band profiles at the heterojunction was determined not only by the Fermi levels in the two semiconductors but also by their relative electron affinities (see fig. 1). The heterojunction

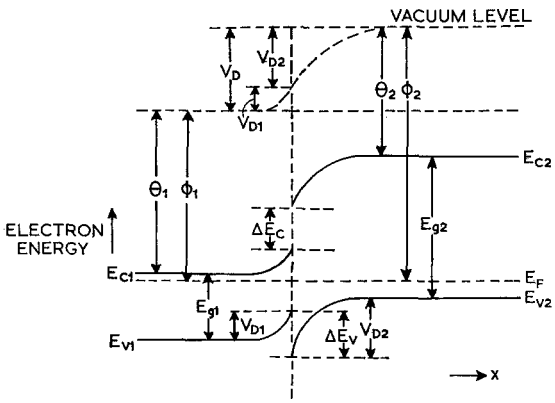

Figure 1 Energy-band diagram of n-p heterojunction at equilibrium (after Anderson).

was considered to be abrupt with a discontinuity at a single line of atoms.

Application of Shockley's homojunction diffusion theory, along with a diode emission model was sufficient to predict the saturation current and current-voltage characteristics of Ge-GaAs heterojunctions. Deviations from this model were explained by the inclusion of a transmission coefficient.

This model ignored effects due to interface states. This was shown to be justifiable by Esaki *et al* [37, 38] from field-effect measurements on the same junction. This is to be expected since the lattice mismatch between Ge and GaAs is small, giving very few free bonds at the interface.

Anderson indicated that his model would be modified by tunnelling effects, image effects, and carrier generation and recombination. The lowering of the potential barrier due to the first two was given [10]; image effects were also considered by Hampshire and Wright [40]. The model was extended by Oldham and Milnes [29] to cover graded heterojunctions.

4.2. Perlman and Feucht's Theory

After assuming the heterojunction band structure proposed by Anderson, Perlman *et al* [46] used a classical, kinetic, emission model to predict the current-voltage characteristics of an abrupt p-n heterojunction. This took into account the effect of changes in electron affinity, electron effective mass, dielectric constant, and band gap at the junction.

The p-n heterojunction was found to have two operating modes, one similar to a homojunction, where minority-carrier build-up at the depletion-region edge limits current, and another similar to a metal-semiconductor junction, where the current is limited by a potential barrier in the n-type semiconductor. On increasing the forward bias, the homojunction mode of operation changes to the metal-semiconductor mode.

The predictions of this model differ from that of Anderson in several respects. Anderson, from the slope of his current-voltage characteristics, recognised two modes of operation, but the saturation currents of both were given as equal to Shockley's saturation current for the p-n homojunction. The transition voltage between the modes was the bias which reduced the reverse barrier to zero. Perlman's theory predicts a transition voltage greater than this value. To fit Anderson's theory to the observed results, a transmission coefficient was required for both types of operation. Perlman indicated that no coefficient would be necessary for metal-semiconductor-type operation, since the current is not limited by the reflection of carriers at the discontinuity, but more by their ability to diffuse away from the junction.

The more rigorous treatment presented by Perlman and Feucht is still limited by their neglect of interface states.

4.3. Oldham and Milne's Theory

The effect of interface states was first included by Oldham *et al* [44] who considered abrupt heterojunctions with edge dislocations at the interface. For mismatches of the order of 2 to 4%, the dislocations were assumed to lie in a

sheet and to be similar to grain boundaries. They concluded that the interface resembles a low-density free surface with edge dislocations producing deep states in the gap. These states are expected to produce two effects, band bending and recombination of excess minority carriers. In the Oldham and Milnes model for n-n structures (see fig. 2), the acceptor nature of the interface states resulted in depletion regions on both sides of the heterojunction. This gives a structure similar to a semiconductor-metal-semiconductor sandwich, except that carriers may traverse the interface region without contacting the interface states.

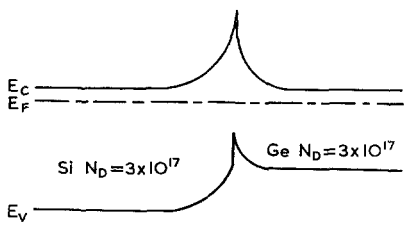

Figure 2 Equilibrium energy-band diagram at Ge-Si n-n heterojunction including interface states (after Oldham and Milnes).

Current-voltage characteristics were derived using a kinetic model which neglected image and tunnelling effects; these showed a double saturation. This was confirmed in their experiments on n-n Ge-Si heterojunctions. The model has been successfully used by Donnelly *et al* [89] to explain certain optical characteristics of Ge-Si heterojunctions.

4.4. Van Ruyven, Papenhuijzen, and Verhoeven's Theory

A more general theory than that of Oldham [44] has been formulated by Van Ruyven *et al* [83]. The interface was considered to be similar to two semiconductors, each with a free surface. Interface states were thought to play a decisive role since they can store sufficient charge to make the surface behave like a thin, metal layer. Contact between the two different surfaces leads to the formation of a dipole layer. Hence the heterojunction consists of three separate junctions: a Schottky barrier between the first semiconductor and its own metal-like surface, a metal contact between two planes of surface states containing a dipole, and another Schottky barrier between the metal-like surface of the second semiconductor and the second semiconductor itself (see fig. 3). This model is the other extreme to that of Anderson. For sufficiently large interface-state densities, the Fermi level at the interface can be fixed near mid-gap, its position being determined by the work function of the free semiconductor surface and being independent of the Fermi-level position in the bulk. Experiments on the photoelectric effect in Ge-GaP heterojunctions provide support for this model.

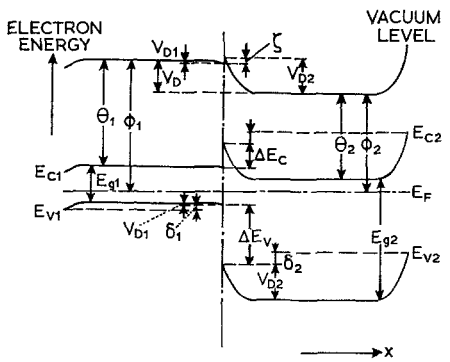

Figure 3 Band profile of a Ge-GaP heterojunction: general case (after Ruyven *et al*).

Other theories have been put forward, but these are of more limited application than those described, e.g. Rediker *et al* [47] found that a tunnelling mechanism explained the observed current-voltage characteristics of their interface alloy heterojunctions.

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Notation

Subscripts 1 and 2 refer to materials 1 and 2 respectively.

$E_{c1,2}$	conduction band edge
$E_{v1,2}$	valence band edge
$R_{g1,2}$	width of forbidden gap
ΔE_c	discontinuity of the conduction band
ΔE_v	discontinuity of the valence band
$V_{D1,2}$	partial built-in voltages
V_D	total built-in voltage
$\phi_{1,2}$	work function in the bulk
$\phi_{s1,2}$	work function at the free surface
$\theta_{1,2}$	electron affinity
$\delta_{1,2}$	difference between overall Fermi level and the Fermi level in the case of complete stabilisation at the surface
ζ	energy jump across the electric dipole formed by interface states