Handout 7

Bandstructure engineering

7.1 Introduction

We shall explore some of the ways in which bands with desired properties can be engineered using what has been termed "chemical architecture". A very simple example of this is the use of *semiconductor alloys*, in which a wide-gap semiconductor and a narrow-gap semiconductor are combined to give a substance with a desired intermediate bandgap. A second example is the *semiconductor superlattice* or *heterostructure*; here, very thin layers of different semiconductors are superimposed.

7.2 Semiconductor alloys

The previous lectures mentioned the fact that direct-gap semiconductors are used in opto-electronic applications. Many of these applications involve the emission of light by recombination of an electron and a hole across the band gap, or absorption of light of the band-gap energy to create an electron-hole pair and hence produce some form of photoconduction;[1] The size of the band gap is therefore of great importance.

Figure 8.1 shows the band gaps and lattice parameters for some of the more common elemental and binary semiconductors. The band gaps available are not generally optimised for practical devices. A desire to improve on this has led to the field of *bandstructure engineering*, where a variety of artificial structures are used to provide bandstructure optimised to a particular application.

The simplest bandstructure engineering involves making *ternary alloys* such as (Ga,Al)As and (Hg,Cd)Te in order to achieve a desired band gap. I list three examples of the uses of such alloys.

$Ga_{1-x}Al_xAs$ is technologically important because GaAs and AlAs form a solid solution over the entire ($0 \leq x \leq 1$) composition range with very little variation of lattice parameter (see Figure 8.1); this means that multilayers of very high quality can be fabricated (see below). A variable direct band gap is obtained for the range $0 \leq x \leq\sim 0.35$; for $x \geq\sim 0.35$ the band-gap is indirect.

The band gap of $Ga_{1-x}In_xAs$ may be adjusted over an energy range which coincides with the low-attenuation region of many optical fibres.

$Hg_{1-x}Cd_xTe$ continues to be of great importance in the fabrication of infrared detectors covering the 10 μm ($x = 0.2$; $E_g \approx 100$ meV) and 5 μm ($x = 0.3$; $E_g \approx 200$ meV) atmospheric windows (regions where the atmosphere has little absorption). The 10 μm region also contains the peak thermal emission of ~ 300 K things, including human beings, so that there are a variety of medical (thermal imaging), meteorological and more sinister applications. Exhausts and jet engines emit well in the 5 μm range, and so the applications of $Hg_{1-x}Cd_xTe$ with $x = 0.3$ can be easily imagined.

[1] See *e.g.* *Semiconductor Physics*, by K. Seeger (Springer, Berlin 1991) Chapters 12 and 13; *Optical Properties of Solids* by Mark Fox, (Oxford University Press, Oxford 2001), *Low-Dimensional Semiconductor Structures*, by M.J. Kelly, (Clarendon Press, Oxford 1995) Chapter 18.

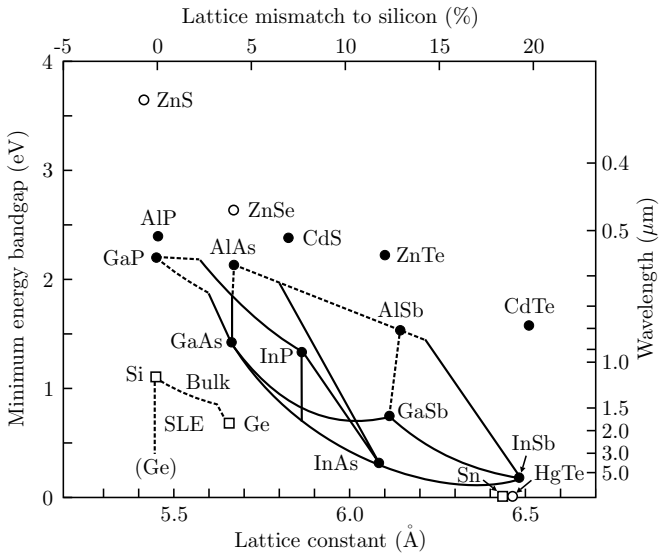

Figure 7.1: Band gap versus lattice parameter for some of the more common semiconductors. The curves indicate commonly-used alloys such as (Ga,Al)As, (Ga,In)As *etc.*; solid curves represent direct gaps and dashed curves indirect gaps.

7.3 Artificial structures

We now turn to a variety of structures which can be grown using techniques developed over the past twenty years or so.

7.3.1 Growth of semiconductor multilayers

The growth of high-quality semiconductor multilayers is described as *epitaxial* (the word is derived from the Greek words *epi* (upon) and *taxis* (arrangement)). The implication is that layers grow on a suitable single-crystal substrate, continuing the crystal structure of that substrate. The layers are thus supposed to be crystallographically well ordered. Two techniques are commonly used to grow epitaxial layers of semiconductors, *Molecular Beam Epitaxy* (MBE) and *Metal-Organic Vapour-Phase Epitaxy* (MOVPE; also known as OMVPE, MOCVD and OMCVD).

- **MBE** Figure 7.2 shows the main components of an MBE machine. The elements which make up the semiconductors to be grown evaporate from *Knudsen cells* at a rate controlled by the cell temperature; cells are also provided for dopants. The evaporated atoms form a beam which travels towards the substrate. Typically the evaporation rates are such that ∼one monolayer is deposited per second. The composition of the layers is controlled by shutters which can swing in front of each cell in ~ 50 ms, cutting off the beam from that cell. The substrate is kept at a well-defined temperature to ensure that the deposited atoms are reasonably mobile, so that they spread out over the substrate in monolayers rather than forming clusters. The whole chamber must be very well evacuated to prevent spurious dopants entering the layers; typical pressures in an MBE machine are $\sim 10^{-11}$ mbar. A number of *in-situ* diagnostic techniques to monitor the growth of the multilayer are provided.

- **MOVPE** Figure 7.3 shows a schematic of an MOVPE machine. The components of the semiconductor to be grown travel to the substrate as gaseous precursors formed by reacting the elements with organic radicals; the precursors are carried along in a stream of hydrogen. Close to the substrate, which is heated by a radiofrequency coil, the precursors react, depositing the semiconductor on the substrate. A typical reaction is

$$\mathrm{Ga(CH)_3 + AsH_3 \rightarrow 3CH_4 + GaAs.} \tag{7.1}$$

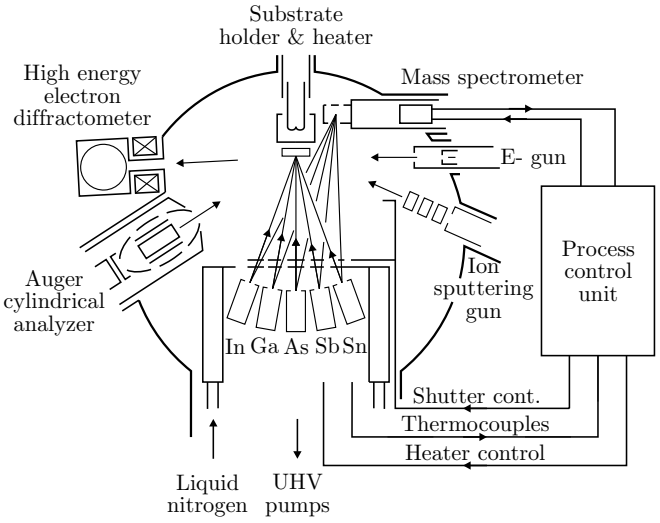

Figure 7.2: Schematic of an MBE machine.

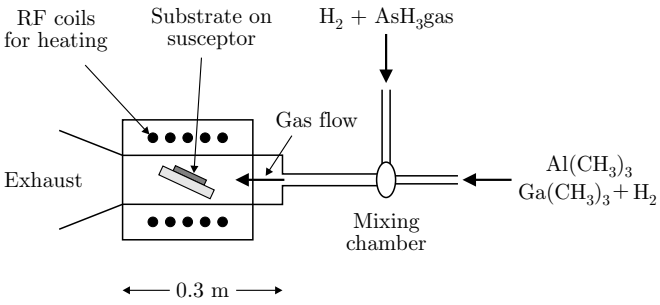

Figure 7.3: Schematic of an MOVPE machine.

Very fast solenoid valves enable the sources of the various components to be switched on and off rapidly.

7.3.2 Substrate and buffer layer

The substrate will be a high quality single crystal, usually of one of the materials to be included in the multilayer. Often the substrate will be *semi-insulating* GaAs (see Section 6.3.8). The first layer to be grown is called the *buffer layer*; it is often the same material as the substrate (but undoped), and is designed to "smooth out" the lumps and bumps of the latter, to provide an atomically-smooth top surface on which to grow the active parts of the multilayer. More recently, *superlattice buffers* consisting of alternating thin ($\sim 1-2$ nm) layers of *e.g.* GaAs and AlAs have sometimes been used for this purpose.

7.3.3 Quantum wells

The simplest multilayer system or *heterostructure* (*hetero* = more than one; *i.e.* the structure is made up of more than one semiconductor) is the *quantum well*. A thick (several hundred nm) layer of a wider gap material such as (Ga,Al)As is grown (the barrier material), followed by a $\sim 2-100$ nm layer of a narrower gap material such as GaAs (the well), followed by another thick layer of wider gap material. Figure 7.4 shows the resulting conduction and valence-band edges; the relative heights of the discontinuities in the conduction- and valence-band edges are instrinsic properties of the two materials involved.

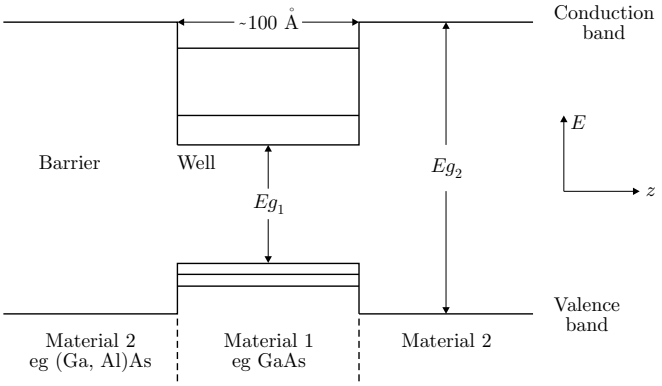

Figure 7.4: Band edges in a quantum well as a function of distance in the growth direction z. The energies of the subbands within the well are shown schematically.

The narrower-gap material forms a one-dimensional potential well in the conduction and valence bands; thus, in the z (growth) direction, the electron and hole levels are bound states of the well, known as *subbands*. The well will contain three sets of subbands,

- the electron subbands,
- the light hole subbands and
- the heavy hole subbands,

each subband within a set being labelled by a quantum number $i = 1,\ 2,\ 3.....$ Motion in the xy plane will be unrestricted; we therefore have a two-dimensional carrier system in the well.

7.3.4 Optical properties of quantum wells

The interband optical absorption or emission of a quantum well will be caused by transitions between hole and electron subbands. The selection rules are determined by the overlap between the electron and hole wavefunctions. Wavefunctions of the same quantum number (or quantum numbers differing by two) will have similar (spatial) shapes and the transition will be strong; wavefunctions whose quantum numbers differ by one will be of opposite symmetry, and so transitions between them will be weak. In summary, the selction rules are[2]

- $\Delta i = 0, 2$: strong, allowed transitions;
- $\Delta i = 1$: weak, "forbidden" transitions.

As there are two sets of hole subbands, strong transitions will occur in pairs, *e.g.* (ith heavy-hole subband to ith electron subband) and (ith light-hole subband to ith electron subband). Figure 7.5 shows the optical absorption of a set of quantum wells of differing well width. The wells are of rather low quality, so that individual transitions are hard to distinguish. However, it is plain that

- the transition energies increase as the wells get narrower, due to the increased subband confinement energy;
- the absorption increases in steps, reflecting the step-like form of the electron-hole joint density of states in two dimensions;
- excitons are very prominent, because the confinement in the well enhances the exciton binding energy by holding the electron and hole closer together than in the bulk semiconductor.

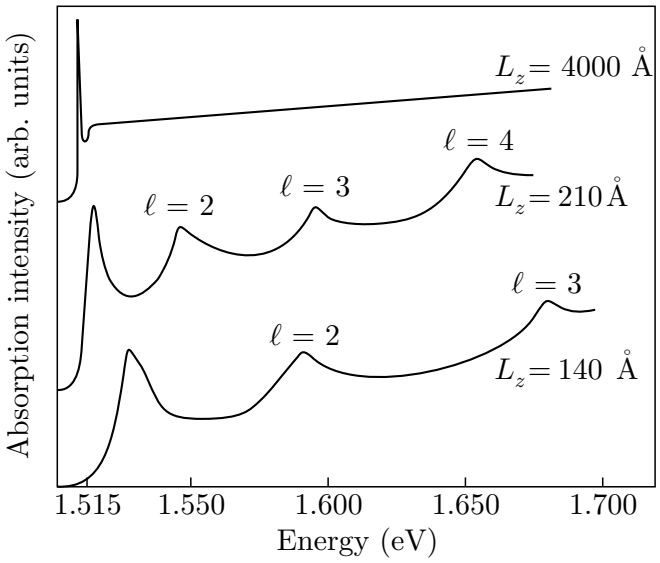

Figure 7.5: Optical absorption of a series of GaAs-(Ga,Al)As quantum wells of differing widths L_z at 4.2 K. (After R. Dingle *et al.*, *Phys. Rev. Lett.* **33**, 827 (1974).)

Figure 7.6 shows the transmission of a set of much higher quality GaAs-(Ga,Al)As quantum wells. Unfortunately the detector used did not give a flat response so that the steps in absorption cannot be seen so clearly; however, the pairs of strong transitions can now be resolved. Note that the excitons involving light holes are almost as strong as excitons involving heavy holes (*c.f.* the bulk case (Figure 6.9), where the latter dominate); this is because quirks of the valence-band bandstructure give the light-hole subbands quite a large in-plane (xy) effective mass, and therefore a large density of states, comparable to that of the heavy holes.

7.3.5 Use of quantum wells in opto-electronics

There are several reasons for the use of quantum wells in opto-electronic applications, *e.g.*

- the energy of the fundamental optical transition can be varied by varying the well width;
- the heavy and light hole degeneracy at the Brillouin-zone centre is broken, removing complications associated with scattering *etc.*;
- all of the transitions are excitonic (*i.e.* sharp features at a well-defined energy, rather than broad edges), even at 300 K;
- the well can be used to hold electrons and holes in close proximity, to encourage more efficient recombination in *e.g.* lasers and LEDs.[3]

Applications include the *Quantum-confined Stark effect modulator*, which is dealt with in detail in *e.g. Low-Dimensional Semiconductor Structures*, by M.J. Kelly, (Clarendon Press, Oxford 1995) Section 18.8.

7.3.6 Superlattices

A *superlattice* contains a set of quantum wells which are sufficiently closely spaced for the carriers to tunnel between wells (see Figure 7.7). The situation is analogous to the tight binding or Kronig–Penney models of bandstructure; the subbands will broaden out to form *minibands* with *minigaps* between. One

[2]For a detailed derivation of these selection rules, see M. Fox, *Optical Properties of Solids*, (OUP, 2000).
[3]See *Semiconductor Physics*, by K. Seeger (Springer, Berlin 1991) Section 13.2.

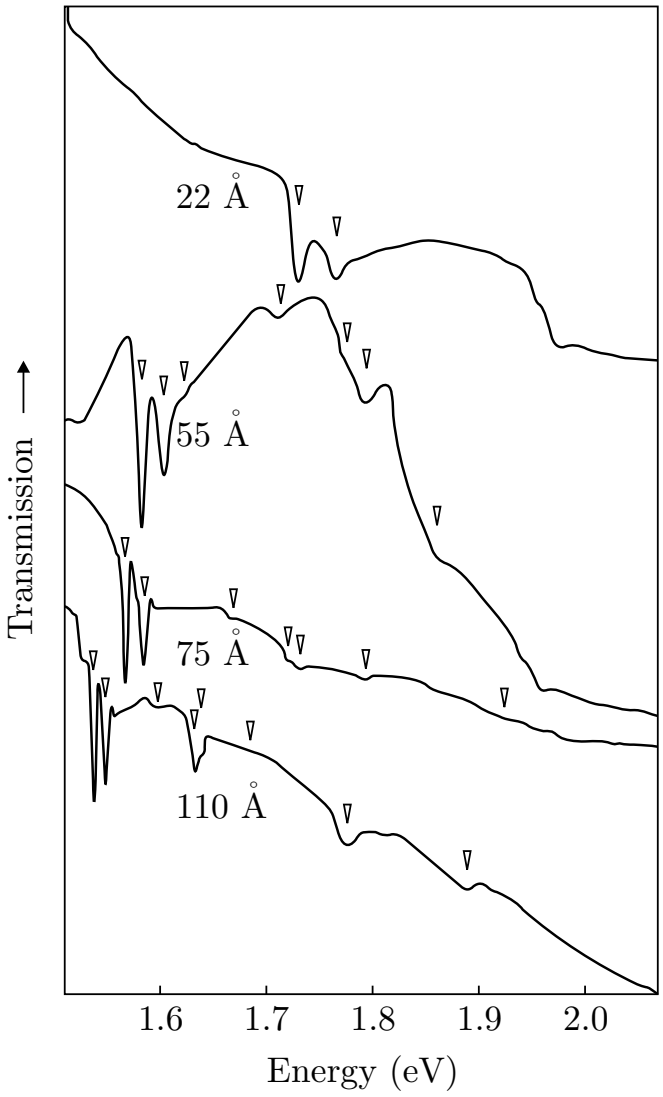

Figure 7.6: Optical absorption of a series of GaAs-(Ga,Al)As quantum wells of differing widths L_z at 55 K. (Data from D.C. Rogers *et al*, *Phys. Rev. B.* **34**, 4002 (1986).)

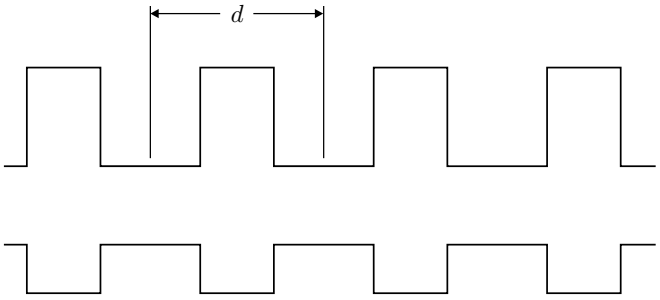

Figure 7.7: Schematic of the band edges in a superlattice.

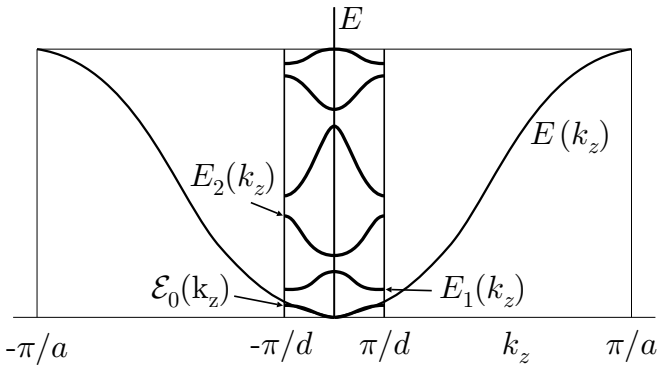

Figure 7.8: Minibands and minigaps in a superlattice (see Figure 7.7). Here, π/a denotes the Brillouin-zone boundary of the underlying lattice; $E(k_z)$ represents the unperturbed, original bulk band. The effect of the superlattice, of period d, is to introduce new "mini Brillouin zones" with boundaries at $\pm\pi/d$. The band is split into *minibands* with dispersion relationships labelled by $E_0(k_z)$, $E_1(k_z)$, $E_2(k_z)$ *etc.*.

can also think of the periodicity of the superlattice introducing a new set of Brillouin-zone boundaries and hence energy gaps (see Figure 7.8).

Superlattices have a variety of applications in *resonant tunnelling structures* and far-infrared detectors; we shall discuss more of the details of these devices in a later lecture.[4]

7.3.7 Heterojunctions and modulation doping

A heterojunction is a single junction between two layers of different semiconductors. A typical example is the GaAs-(Ga,Al)As heterojunction. First, a thick layer of undoped GaAs is grown, followed by a few tens of nm of (Ga,Al)As (the *spacer layer*). After this a section of heavily-doped ($n \sim 10^{18}$ cm^{-3}) (Ga,Al)As is deposited, followed by more undoped (Ga,Al)As (not shown). The final band arrangement is shown in Figure 7.9. The combination of the conduction band offset at the interface and the pinning of the chemical potential inside the GaAs and (Ga,Al)As layers results in a one-dimensional, approximately triangular potential well containing electrons which have "dropped off" the donors in the (Ga,Al)As. As in the case of the quantum well, the electrons' z-direction motion is quantised into subbands; however, the xy motion is unconstrained, so that a degenerate (metallic) two-dimensional electron system results.

The spacer layer separates the ionised donors from the electrons, dramatically reducing the scattering; low-temperature mobilities $\mu_c \sim 10^7 \mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$ are possible using this technique, which is known as *modulation doping* (because the dopant concentration in the (Ga,Al)As is modulated).

Applications of heterojunctions include the *High-Electron-Mobility Transistor* (HEMT), an FET with a heterojunction as active layer.[5] Most experiments on the *Quantum Hall Effect* are carried out using heterojunctions; we shall study this effect in detail later.

Other applications of modulation doping include the fabrication of so-called δ-doping layers, in which a very heavy dose of dopant atoms is deposited in a small width ($\sim$ a few monolayers). In effect, this forms a two-dimensional impurity band, a very thin metallic layer within the host semiconductor. Such layers are finding applications as metallic gates and contacts *within* complex, layered semiconductor structures.

7.3.8 The envelope-function approximation

The *envelope-function approximation* is often used to calculate the electronic energy levels in heterostructures, such as GaAs-(Ga,Al)As quantum wells, which are made up from two or more similar semiconductors. Because the two semiconductors involved are very similar from both chemical and

[4] See also See *Low-Dimensional Semiconductor Structures*, by M.J. Kelly, (Clarendon Press, Oxford 1995) Chapters 9 and 10, 17-19.

[5] See *Low-Dimensional Semiconductor Structures*, by M.J. Kelly, (Clarendon Press, Oxford 1995) Chapter 16.

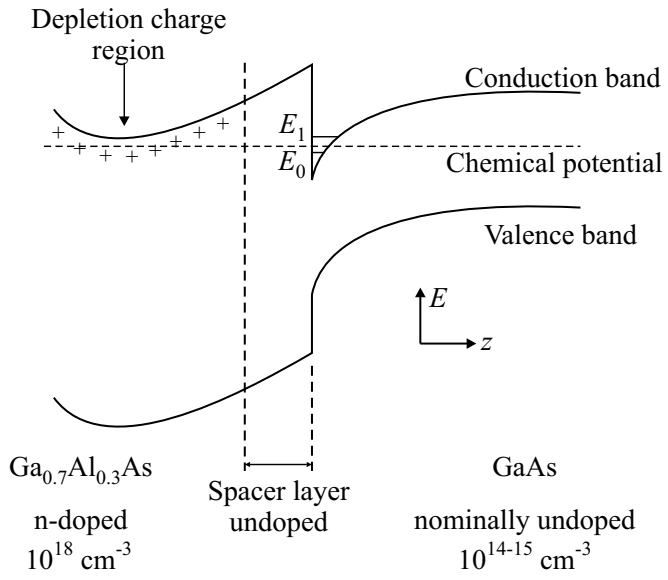

Figure 7.9: The band edges in a modulation-doped GaAs-(Ga,Al)As heterojunction.

crystallographic points of view, it is assumed that the rapidly-oscillating part of the Bloch function (the part which has the periodicity of the lattice) is the same in both materials; only the *envelopes* ϕ of the Bloch functions differ in the two semiconductors.

As an example, consider the GaAs-(Ga,Al)As quantum well shown in Figure 7.4; let a typical envelope function in the GaAs well be $\phi_{\rm A}(z)$ and the corresponding envelope function in the (Ga,Al)As barriers be $\phi_{\rm B}(z)$. The boundary conditions in the Envelope Function Approximation at the interfaces (*i.e.* at $z = \pm\frac{a}{2}$) are

$$\phi_{\rm A} = \phi_{\rm B} \tag{7.2}$$

and

$$\frac{1}{m^*_{\rm A}}\frac{{\rm d}\phi_{\rm A}}{{\rm d}z} = \frac{1}{m^*_{\rm B}}\frac{{\rm d}\phi_{\rm B}}{{\rm d}z}, \tag{7.3}$$

where $m^*_{\rm A}$ and $m^*_{\rm B}$ are the effective masses in the well and barrier respectively. Equation 7.3 ensures that the probability-density flux is conserved.

By considering envelope functions such as $\cos(kz)$ and $\sin(kz)$ in the well and evanescent waves $e^{\pm\kappa z}$ in the barriers, the subband energies can be found. The problems contain an example of this technique, which can easily be extended to more complex structures such as superlattices.