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Large-Bandgap Semiconductors

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Abstract

The general features of large-bandgap semiconductors that make them interesting for electronic and optoelectronic applications are briefly reviewed. The nitrides AIN, GaN and InN are singled out for a more focused treatment.

General Features

The size of the energy-gap between valence and conduction states in a solid determines many of the solid's properties. The most directly affected are the optical properties; in particular, the energy of the photon that can interact with the valence electrons. Small-bandgap semiconductors such as InSb and InAs find application as detectors in the medium-to-far infrared; medium-bandgap semiconductors such as GaInAs are used in optical communication systems where the photon energy corresponds with that for minimum absorption of near infrared light in optical fibers Large-bandgap semiconductors ($E_g \geq 2eV$) come into their own in the manipulation of visible and ultraviolet light.

Another important affect of the size of the energy gap is on the temperature dependence of the population of electrons in the conduction band. This population must be kept low in photodetectors so that the effect of photoexcited electrons is large, and this means that small-bandgap semiconductors can work only at low temperatures. In electronic devices the population of electrons must be largely independent of temperature and determined by doping, conditions that are easily fulfilled in the case of Ge, the workhorse Si and Ga As at room temperature, and a fortiori in the case of large-bandgap materials. Large-bandgap semicondutors have the added advantage in that they can support higher electric field before breaking down, which means that they can be used for high-power electronic devices.

The energy gap between valence and conduction states in a binary semiconductor depends upon a number of factors [1], the principle ones being the distance apart and the electronegativity of the component atoms in the crystal lattice. Large bandgaps are associated with small interatomic spacing and large differences of electronegativity. Nitrogen

is a small atom and highly electronegative and so is an ideal constituent for a III-VI large-bandgap semiconductor. Oxygen is also a small atom and is even more electronegative than nitrogen, so this is an ideal constituent for II-VI compounds. All the halogens are highly electronegative with fluorine best of all, so, coupled with the low electronegativities of the alkaline metals it is not surprising that the alkali halides have such large bandgaps that they are usually classified as insulators rather than semiconductors. Of the group IV semiconductors diamond qualifies as a large-bandgap material on the ground solely of small atomic size and SiC qualifies on ground both of atomic size and polarity (C is significantly more electronegative than Si). It should be noted that in the case of atoms from the row in the periodic table containing silicon and those above, the energy gap tends to be indirect, with the X valley being the lowest of the conduction-band valleys. Nevertheless, all the nitrides have a direct gap.

Apart from diamond, all large-bandgap semiconductors are polar and have zinc-blende or wurtzite crystal lattices. Neither of these lattices have a centre of inversion and so all of these materials are piezoelectric. It follows that the transport of electrons and of holes in these materials will be deeply affected by polar interactions with the lattice vibrations. Since the atoms involved are small and light, the optical-phonon energy is high ($\approx$100meV), so few optical phonons are excited at room temperature, which moderates the scattering rate and offers greater opportunity for ballistic transport. Elsewhere, the strong polar interaction causes appreciable Franck-Condon effects associated with the optical properties of trapped electrons [2].

The response to high applied electric fields is of considerable interest for the design of high-power microwave devices. In direct-gap materials it can be expected that the hot-electron behaviour will be dominated by the unstable effects of electron-transfer into the X and L valleys. High-power Gunn devices are therefore possible. In indirect-gap materials, where this effect does not occur, or in direct-gap materials in which NDR instabilities are suppressed, the large bandgap can be expected to inbihit breakdown up to fields of order 1MV/cm and above, and this makes the development of high-power IMPATT devices potentially important. However, there exists a fundamental lack of understanding of how breakdown occurs in large-bandgap materials-impact ionization being only one possible mechanism. This problem goes back to well before transistors were invented and it remains an active research area today. Its essence is that once an electron requires an energy of 3eV or more to impact ionize, the presence of a field high enough to produce that energy allows other mechanisms to enter, for example, atoms can be knocked out of the lattice, Wannier-Stark ladders may form, ionic conduction can take place, non-uniformities at the electrodes can play a crucial rôle. And basic to all of this is the problem of describing the motion of an electron with energy several electron volts above the conduction-band edge in the presence of the periodic potential of the lattice.

The fabrication of heterostructures consisting of large-bandgap semiconductors brings in other factors. First of all, the band-edge discontinuities can be 1eV or more, and so it is possible to form deep quantum wells in which concentrations of electrons of order 10^{13} cm^{-2} are possible, promising, once more, high-power transistor action. The large bandedge discontinuities also offer the possibility of hot-electron injection in transistors.

More interesting are the effects of electric polarization. For many of the large-bandgap polar semiconductors, and this includes the nitrides, the thermodynamically favoured crystals structure is that of wurtzite. This structure is special in that it is the highest symmetry structure to allow spontaneous electric polarization to occur [3]. This immediately makes the nitrides very different from conventional III-V semiconductors. Moreover, they exhibit large piezoelectric effects, for example, associated with the elastic strain arising from the lattice mismatch. Large electric fields can be produced by spontaneous and strain-induced polarization and these can be exploited in order to produce substantial screening populations of electrons, thereby eliminating the need to use dopants. These effects can also be used to produce Stark effects in superlattices. The appearance of spontaneous polarization makes the III-V nitrides and the II-VI oxides more like conventional ferroelectric materials such as perovskite [4].

Further advantages over conventional semiconductors are (a) a comparatively low permittivity (useful in milimetre-wave amplifiers in reducing parasitic capacitance) and, for bandgaps in excess of around 5eV, (b) a negative electron affinity (useful for exploitation as cold cathodes). Furthermore, the high Debye temperature implies good thermal conductivity at room temperature in pure, isotope-free material, another advantage for high-power applications. In pure material thermal conductivity is limited by umklapp processes and scattering by isotopes via mass differences. In the case of the nitrides the latter contribution is expected to be small at room temperature. Al has no isotopes and N has two but one in only small concentration, so ALN can be regarded for all practical purposes as isotope-free. Ga and In each have two but their effect will be diluted by the coupling with N and certainly too weak to affect the conductivity at the elevated temperatures expected in highpower operation.

Table 1. Some properties of the Nitrides

	AIN	GaN	InN
a(Å)	3.110	3.190	3.544
c(Å)	4.980	5.189	5.718
u(Å)	1.90	1.96	2.16
ρ(g/cm^3)	3.26	6.15	6.81
E_g(direct) (eV)	6.28	3.39	1.89
E_g(indirect) (eV)	7	5.39	4.09
$\hbar\omega_L$ (meV)	113	92	89
$\varepsilon_s/\varepsilon_0$	9.14	8.9	15.3
$\varepsilon_\infty/\varepsilon_0$	4.76	5.35	8.4
e_{31}	-0.60	-0.49	-0.57
e_{33}	1.46	0.73	0.97
P_3(sp) (C/m^3)	-0.081	-0.029	-0.032
V_{SL} (10^5 cm/s)	10.4	6.56	6.24
V_{sT} (10^5 cm/s)		2.68	2.55
Ξ (eV)		8.3	7.1

The low-field electron mobility in GaN

Proper epitaxial growth of the III-V nitrides has been hampered by the lack of a suitable substrate. This will, no doubt, change in the near future, but crurrently, MBE, and less so OMVPE, material, grown on sapphire, suffers from the presence of an array of dislocations. This has not prevented the fabrication of working devices-blue laser [5] and HEMT [6]-but it is too early for theoretical predictions of the behaviour of ideal material to be usefully compared with experiment. For example, the predicted value at room temperature for the electron mobility associated purely with polar-optical-phonon scattering in GaN (wurtzite) at low electron densities is 2,200cm^2/Vs (m^*=0.22m_0) or 2,500cm^2/Vs (m^*=0.20m_0) [7] (there is still some uncertainty surrounding the effective mass), but measured Hall mobilities are much lower (typically 1,000cm^2/Vs). (Note that the Hall factor has not been determined but it is not expected to be far from unity.)

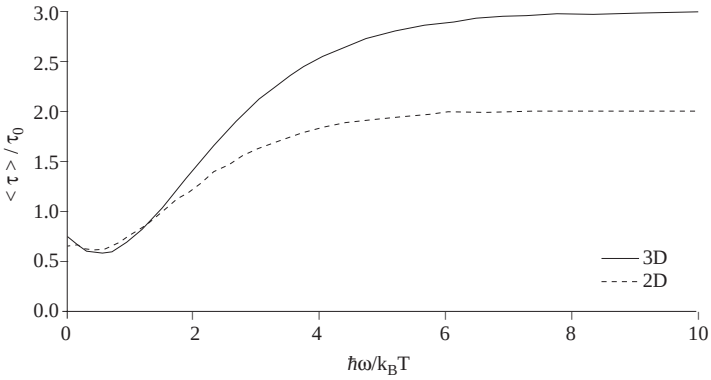

Figure 1. Ratio of averaged momentum-relaxation time-constants of the drifted and standard models [8].

The large optical-phonon energy of GaN (92 meV) makes scattering by optical phonons sensitive to the degree of electron-electron scattering at room temperature [8]. In this respect it differs markedly from GaAs. This can be illustrated most simply by first calculating the mobility predicted on the assumption that an effective relaxation time can be defined associated solely with phonon absorption (which turns out to be an excellent approximation at low densities) and comparing it with the mobility calculated on the assumption that electron-electron scattering maintains a drifted-Fermi-Dirac distribution. In the case of GaAs there is very little difference; in the case of GaN the assumption of a drifted F-D distribution gives a mobility nearly three times higher (Figure 1.) However, when the Boltzmann equation is solved exactly in the *absence* of electron-electron scattering but taking account of the effects of degeneracy, it is found that the mobility *falls* with increasing degeneracy [9]. This occurs because as the Fermi level increases more electrons have energies to emit phonons and emission is so much more rapid than absorption that it overcomes eqclusion effects. Thus, increasing the electron population reduces the

mobility through degenereacy effects but increases the mobility through electron-electron scattering. The net effect, as described in terms of a simple model, is shown in Figure 2. The reduction of mobility with increasing electron density is an unwanted feature for power devices.

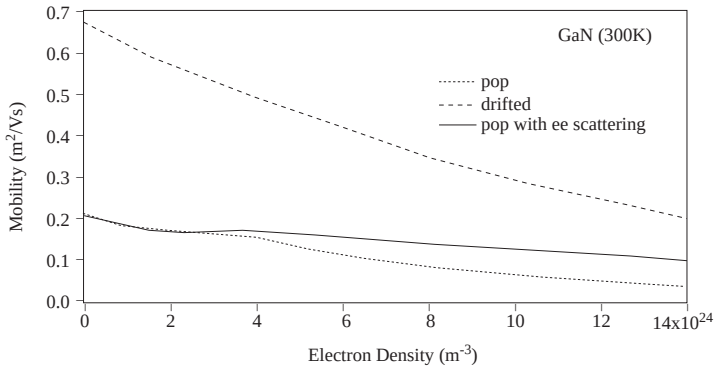

Figure 2. Electron mobility versus electron density [9].

Phonon lifetime

The speed of GaN devices, lasers or transistors, will be determined, in part at least, by the rate at which the energy of carriers, gained by injection or from the applied field, relaxes. The major mechanism for this at room temperature is via the emission of optical phonons. Since optical phonons, once emitted, can be reabsorbed it is of some importance to establish their lifetime. The longer the lifetime the hotter will be the part of the phonon population that interacts with the carriers and the slower will be the net energy relaxation rate. Optical phonons decay to other phonons via the anharmonicity of the lattice. Since the work of Klemens in this area [10] it had been thought that an LO phonon decayed to two LA phonons each of half the frequency of the LO mode. However, this process is energetically impossible in GaN on account of the large frequency gap between optical and acoustic modes, which occurs as a consequence of the mass disparity between Ga and N. It turns out that the energetically allowed process is LO→TO+(LA or TA) [11]. The estimated lifetime for this process is a few picoseconds. These predictions have been confirmed experimentally [12]. Hot-phonon effects in GaN are therefore not expected to be significantly different from those in GaAs.

Polarization

A typical nitride HEMT has 300 Å of undoped $Al_{0.3}Ga_{0.7}N$ grown on top of a thick GaN layer on sapphire. In this configuration the c axis is vertical and is denoted [0001] if the Ga face is uppermost and $[000\overline{1}]$ if the N face is uppermost. Both the GaN and the AlGaN are electrically polarized. (In the equivalent structure with AlGaAs on GaAs,

grown along the [100] direction, there would be by no polarization.) The Polarization in the GaN is caused by the spontaneous polarization that the wurtzite structure exhibits, and that in the AlGaN is composed of the sum of the spontaneous polarization and the polarization caused by the elastic strain via the piezoelectric effect. Electric fields of order MV/cm can be generated. These have the effect of attracting charge at the surface and at the interface which act to partially screen the fields. Given the right sign of polarization in the structure a large density of electrons can be induced at the heterojunction without the need of donors. Thus, in principle, charged-impurity scattering can be eliminated. The sign of these polarization effects depends on whether the layer is Ga-faced or N-faced. Growth by MOCVD on sapphire tends to grow in the [0001] (Ga-faced) direction whereas MBE growth is in the $[000\bar{1}]$ (N-faced) direction, and different properties are observed.

The calculation of spontaneous polarization and piezoelectric coefficients calls for sophisticated quantum theoretical methods to determine total energy and its minimization. The results of a recent calculation of the spontaneous polarization [4] are shown in the table.

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