1 Introduction

The proper conduct of science
lies in the pursuit of Nature's puzzles,
wherever they may lead.
J.M. Bishop [1]

The historic development of semiconductor physics and technology began in the second half of the 19th century. Interesting discussions of the early history of the physics and chemistry of semiconductors can be found in treatises of G. Busch [2] and Handel [3]. The history of semiconductor industry can be followed in the text of Morris [4] and Holbrook et al. [5]. In 1947, the realization of the transistor was the impetus to a fast-paced development that created the electronics and photonics industries. Products founded on the basis of semiconductor devices such as computers (CPUs, memories), optical-storage media (lasers for CD, DVD), communication infrastructure (lasers and photodetectors for optical-fiber technology, high frequency electronics for mobile communication), displays (thin film transistors, LEDs), projection (laser diodes) and general lighting (LEDs) are commonplace. Thus, fundamental research on semiconductors and semiconductor physics and its offspring in the form of devices has contributed largely to the development of modern civilization and culture.

1.1 Timetable

In this section early important milestones in semiconductor physics and technology are listed.

1782
A. Volta – coins the phrase 'semicoibente' (semi-insulating) which was translated then into English as 'semiconducting' [6].

1821
T.J. Seebeck – discovery of semiconductor properties of PbS [7].

M. Grundmann, *The Physics of Semiconductors*, 2nd ed., Graduate Texts in Physics, DOI 10.1007/978-3-642-13884-3_1,

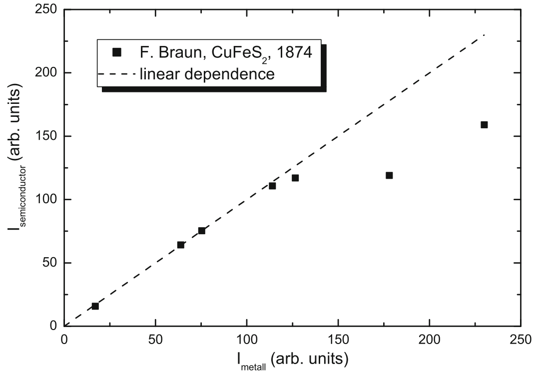


Fig. 1.1. Current through a silver–$CuFeS_2$–silver structure as a function of the current through the metal only, 1874. Data points are for different applied voltages. Experimental data from [12]

1833
M. Faraday – discovery of the temperature dependence of the conductivity of Ag_2S (negative $\mathrm{d}R/\mathrm{d}T$) [8].

1873
W. Smith – discovery of photoconductivity in selenium [9]. Early work on photoconductivity in Se is reviewed in [10, 11].

1874
F. Braun[1] – discovery of rectification in metal–sulfide semiconductor contacts [12], e.g. for $CuFeS_2$ and PbS. The current through a metal–semiconductor contact is nonlinear (as compared to that through a metal, Fig. 1.1), i.e. a deviation from Ohm's law. Braun's structure is similar to a MSM diode.

1876
W.G. Adams and R.E. Day – discovery of the photovoltaic effect in selenium [14].
W. Siemens – large response from selenium photoconductor [15], made by winding two thin platinum wires to the surface of a sheet of mica, and then covering the surface with a thin film of molten selenium. Resistance ratio between dark and illuminated by sunlight was larger than ten [15] and measured to 14.8 in [16].

1879
E.H. Hall – measurement of the transverse potential difference in a thin gold leaf on glass [17, 18]. Experiments were continued by his mentor H.A.

[1]F. Braun made his discoveries on metal–semiconductor contacts in Leipzig while a teacher at the Thomasschule zu Leipzig [13]. He conducted his famous work on vacuum tubes later as a professor in Strasbourg, France.

Rowland [19]. A detailed account of the discovery of the Hall effect is given in [20, 21].

1883
Ch. Fritts – first solar cell, based on an gold/selenium rectifier [16]. The efficiency was below 1%.

1901
J.C. Bose – point contact detector for electromagnetic waves based on galena (PbS) [22]. At the time, the term semiconductor was not introduced yet and Bose speaks about 'substances of a certain class (...) presenting a decreasing resistance to the passage of the electric current with an increasing impressed electromotive force'.

1906
G.W. Pickard – rectifier based on point contact (cat's whisker) diode on silicon [23–25]. Erroneously, the rectifying effect was attributed to a thermal effect, however, the drawing of the 'thermo-junction' (TJ in Fig. 1.2) developed into the circuit symbol for a diode (cmp. Fig. 20.56a).

1907
H.J. Round – discovery of electroluminescence investigating yellow and blue light emission from SiC [26].
K. Bädeker – preparation of metal (e.g. Cd, Cu) oxides and sulfides and also CuI from metal layers using a vapor phase transport method [27].[2]

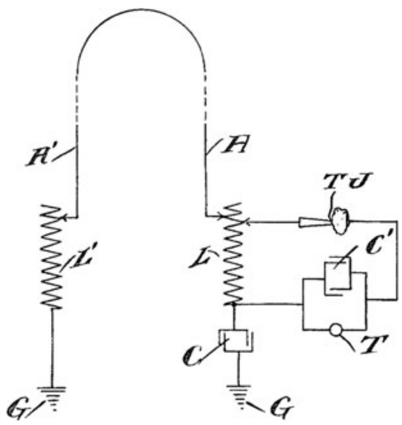


Fig. 1.2. Circuit diagram for a radio receiver with a point-contact diode (TJ). Adapted from [23]

[2]This work was conducted as Habilitation in the Physics Institute of Universität Leipzig. Bädeker became subsequently professor in Jena and fell in WW I. His scientific contribution to semiconductor physics is discussed in [28].

CuI is reported transparent (∼ 200 nm thick films) with a specific resistivity of $\rho = 4.5 \times 10^{-2}\,\Omega\,\mathrm{cm}$, the first transparent conductor.[3] Also CdO (films of thickness 100–200 nm) is reported to be highly conductive, $\rho = 1.2 \times 10^{-3}\,\Omega\,\mathrm{cm}$, and orange-yellow in color, probably the first reported TCO (transparent conductive oxide). Anion deficiency in CuI causes insulating behavior.

1911
The term 'Halbleiter' (semiconductor) is introduced for the first time by J. Weiss [29] and J. Königsberger and J. Weiss [30]. Königsberger preferred the term 'Variabler Leiter' (variable conductor).

1925
J.E. Lilienfeld[4] – proposal of the metal-semiconductor field-effect transistor (MESFET) [33]) (Fig. 1.3). He was also awarded patents for a depletion mode MOSFET [34] and current amplification with nppn- and pnnp-transistors [35].

1927
A. Schleede, H. Buggisch – synthesis of pure, stoichiometric PbS, influence of sulphur excess and impurities [36].
A. Schleede, E. Körner – activation of luminescence of ZnS [37, 38].

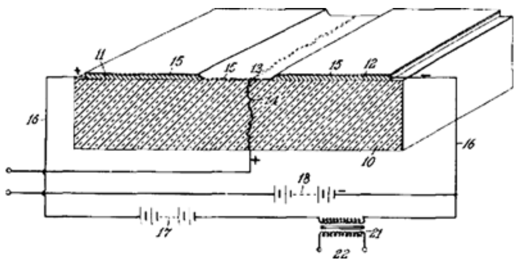


Fig. 1.3. Sketch of a field-effect transistor, 1926. From [33]

[3]CuI is actually a p-type transparent conductor; at that time the reverse sign of the Hall effect could not be interpreted as hole conduction yet although Bädeker considered positive charges [28].

[4]After obtaining his PhD in 1905 from the Friedrich-Wilhelms-Universität Berlin, J.E. Lilienfeld joined the Physics Department of University of Leipzig and worked on gas liquefaction and with Lord Zeppelin on hydrogen-filled blimps. In 1910 he became professor at the University of Leipzig where he mainly researched on X-rays and vacuum tubes. To the surprise of his colleagues he left in 1926 to join a US industrial laboratory [31, 32].

1928
F. Bloch – quantum mechanics of electrons in a crystal lattice, 'Bloch functions' [39].

1929
R. Peierls – explanation of positive (anomalous) Hall effect with unoccupied electron states [40, 41].

1931
W. Heisenberg – theory of hole ('Löcher') states [42].
R. de L. Kronig and W.G. Penney – properties of periodic potentials in solids [43].
A.H. Wilson – development of band-structure theory [44].
C. Zener – Zener tunneling [45].

1933
C. Wagner – excess ('Elektronenüberschuss-Leitung', n-type) and defect ('Elektronen-Defektleitung', p-type) conduction [46]. Anion deficiency in ZnO causes conducting behavior [47].

1936
J. Frenkel – description of excitons [48].

1938
B. Davydov – theoretical prediction of rectification in Cu_2O [49].
W. Schottky – theory of the boundary layer in metal–semiconductor contacts [50], being the basis for Schottky contacts and field-effect transistors.
N.F. Mott – metal–semiconductor rectifier theory [51].
R. Hilsch and R.W. Pohl – three-electrode crystal (KBr) [52].

1940
R.S. Ohl – Silicon-based photoeffect (solar cell, Fig. 1.4) [53] from a pn-junction formed within a slab of polycrystalline Si fabricated with directed solidification due to different distribution coefficients of p- and n-dopants (e.g. boron and phosphorus, cmp. Fig. 4.7b) (J. Scaff and H. Theurer) [54, 55].

1941
R.S. Ohl – Silicon rectifier with point contact [56] (Fig. 1.5), building on work from G.W. Pickard (1906) and using metallurgically refined and intentionally doped silicon (J. Scaff and H. Theurer) [54].

1942
K. Clusius, E. Holz and H. Welker – rectification in germanium [57].

1945
H. Welker – patents for JFET and MESFET [58].

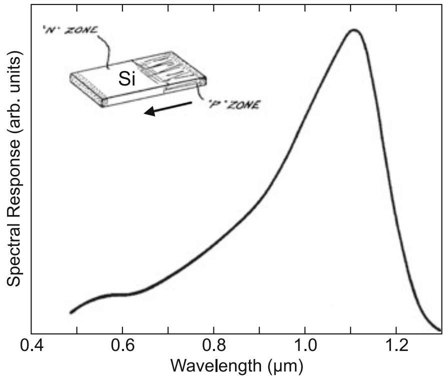


Fig. 1.4. Spectral response of silicon pn-junction photoelement, 1940. The *inset* depicts schematically a Si slab with built-in pn-junction formed during directed solidification (cmp. Fig. 4.7). The *arrow* denotes the direction of solidification. Adapted from [53]

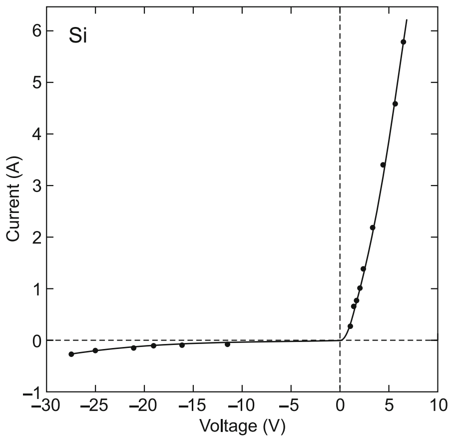


Fig. 1.5. Characteristics of a silicon rectifier, 1941. Adapted from [56]

1947
W. Shockley, J. Bardeen and W. Brattain fabricate the first (point contact) Transistor in the AT&T Bell Laboratories, Holmdel, NJ in an effort to improve hearing aids [59].[5] Strictly speaking the structure was a point-contact transistor. A 50-μm wide slit was cut with a razor blade into gold foil over a plastic (insulating) triangle and pressed with a spring on n-type germanium (Fig. 1.6a) [63]. The surface region of the germanium is p-type due to

[5]Subsequently, AT&T, under pressure from the US Justice Department's antitrust division, licensed the transistor for $25,000. This action initiated the rise of companies like Texas Instruments, Sony and Fairchild.

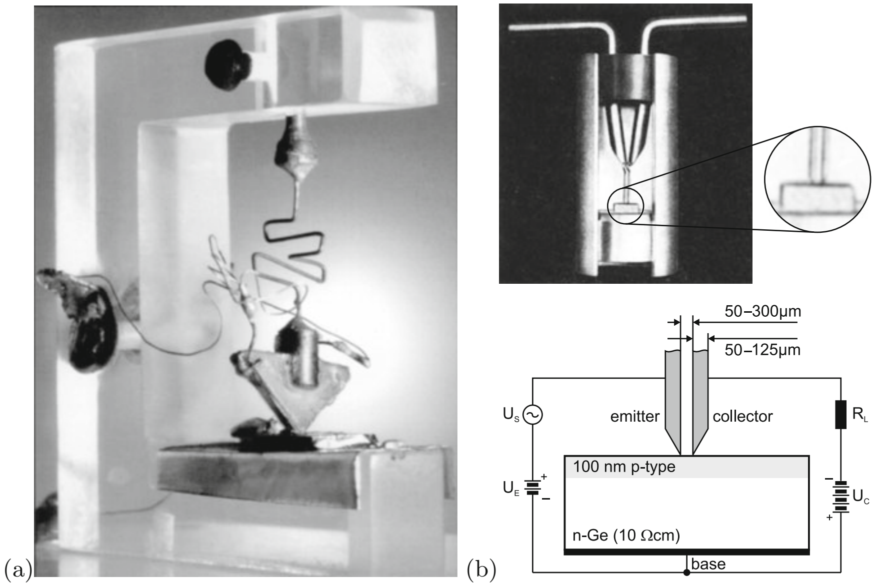


Fig. 1.6. (**a**) The first transistor, 1947 (length of side of wedge: 32 mm). (**b**) Cutaway model of a 1948 point contact transistor ('Type A') based on n-type bulk Ge ($n = 5 \times 10^{14}\,\mathrm{cm}^{-3}$) and common base circuit diagram. The surface region (~ 100 nm depth) of the Ge is p-type due to surface states and represents an inversion layer. The two wires are made from phosphor bronze. Adapted from [61]

surface states and represents an inversion layer. The two gold contacts form emitter and collector, the large-area back contact of the germanium the base contact [61]. For the first time, amplification was observed [62]. Later models use two close point contacts made from wires with their tips cut into wedge shape (Fig. 1.6b) [61].[6] More details about the history and development of the semiconductor transistor can be found in [63], written on the occasion of the 50th anniversary of its invention.

1948
W. Shockley – invention of the bipolar (junction) transistor [64].

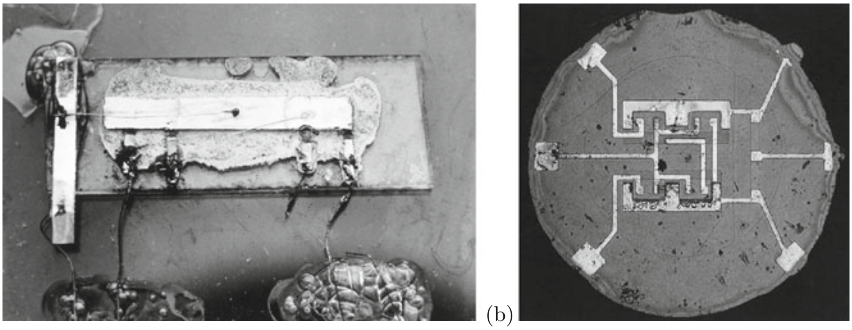
1952
H. Welker – fabrication of compound semiconductors [65–68]
W. Shockley – description of today's version of the (J)FET [69].

---

[6] The setup of Fig. 1.6b represents a common base circuit. In a modern bipolar transistor, current amplification in this case is close to unity (Sect. 23.2.2). In the 1948 germanium transistor, the reversely biased collector contact is influenced by the emitter current such that current amplification $\partial I_\mathrm{C}/\partial I_\mathrm{E}$ for constant U_C was up to 2–3. Due to the collector voltage being much larger than the emitter voltage, a power gain of $\sim$125 was reported [61].

1953
G.C. Dacey and I.M. Ross – first realization of a JFET [70].
D.M. Chapin, C.S. Fuller and G.L. Pearson – invention of the silicon solar cell at Bell Laboratories [71]. A single 2-cm^2 photovoltaic cell from Si, Si:As with an ultrathin layer of Si:B, with about 6% efficiency generated 5 mW of electrical power.[7] Previously existing solar cells based on selenium had very low efficiency (<0.5%).

1958
J.S. Kilby made the first integrated circuit at Texas Instruments. The simple 1.3 MHz RC-oscillator consisted of one transistor, three resistors and a capacitor on a $11 \times 1.7\,mm^2$ Ge platelet (Fig. 1.7a). J.S. Kilby filed in 1959 for a US patent for miniaturized electronic circuits [72]. At practically the same time R.N. Noyce from Fairchild Semiconductors, the predecessor of INTEL, invented the integrated circuit on silicon using planar technology [73]. A detailed view on the invention of the integrated circuit can be found in [74]. Figure 1.7b shows a flip-flop with four bipolar transistors and five resistors. Initially, the invention of the integrated circuit[8] met scepticism because of concerns regarding yield and the achievable quality of the transistors and the other components (such as resistors and capacitors).



(a) (b)

Fig. 1.7. (**a**) The first integrated circuit, 1958 (germanium, $11 \times 1.7\,mm^2$). (**b**) The first planar integrated circuit, 1959 (silicon, diameter: 1.5 mm)

[7] A solar cell with 1 W power cost $300 in 1956 ($3 in 2004). Initially, 'solar batteries' were only used for toys and were looking for an application. H. Ziegler proposed the use in satellites in the 'space race' of the late 1950s.

[8] The two patents led to a decade-long legal battle between Fairchild Semiconductors and Texas Instruments. Eventually, the US Court of Customs and Patent Appeals upheld R.N. Noyce's claims on interconnection techniques but gave J.S. Kilby and Texas Instruments credit for building the first working integrated circuit.

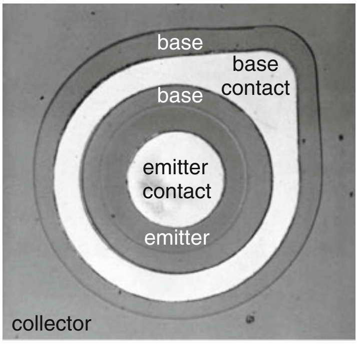


Fig. 1.8. Planar pnp silicon transistor, 1959. The contacts are Al surfaces (not bonded)

1959
J. Hoerni[9] and R. Noyce – first realization of a planar transistor (in silicon) (Fig. 1.8) [76–79].

1960
D. Kahng and M.M. Atalla – first realization of a MOSFET [80, 81].

1962
The first semiconductor laser on GaAs basis at 77 K at GE [82] and at IBM [83]. First visible laser diode [84].

1963
Proposal of a double heterostructure laser (DH laser) by Zh.I. Alferov [85] and H. Kroemer [86].
J.B. Gunn – discovery of the Gunn effect, the spontaneous microwave oscillations in GaAs and InP at sufficiently large applied electric field (due to negative differential resistance) [87].

1966
Zh.I. Alferov – report of the first DH laser on the basis of GaInP at 77 K [88].
C.A. Mead – proposal of the MESFET ('Schottky Barrier Gate FET') [89].

1967
W.W. Hooper and W.I. Lehrer – first realization of a MESFET [90].

1968
DH laser on the basis of GaAs/AlGaAs at room temperature, independently developed by Zh.I. Alferov [91] and I. Hayashi [92].
GaP:N LEDs with yellow-green emission (550 nm) and 0.3% efficiency [93].

[9]The Swiss born Jean Hoerni also contributed $12 000 for the building of the first school in the Karakoram Mountain area in Pakistan and has continued to build schools in Pakistan and Afghanistan as described in [75].

1968
SiC blue LED with efficiency of 0.005% [94].

1975
First monolithic microwave integrated circuit (MMIC) [95].

1995
S. Nakamura – blue GaN heterostructure LED with efficiency exceeding 10% [96].

1.2 Nobel Prize Winners

Several Nobel Prizes[10] have been awarded for discoveries and inventions in the field of semiconductor physics (Fig. 1.9).

1909
Karl Ferdinand Braun
'in recognition of his contributions to the development of wireless telegraphy'

1914
Max von Laue 'for his discovery of the diffraction of X-rays by crystals'

1915
Sir William Henry Bragg
William Lawrence Bragg
'for their services in the analysis of crystal structure by means of X-rays'

1946
Percy Williams Bridgman
'for the invention of an apparatus to produce extremely high pressures, and for the discoveries he made therewith in the field of high pressure physics'

1953
William Bradford Shockley
John Bardeen
Walter Houser Brattain
'for their researches on semiconductors and their discovery of the transistor effect'

1973
Leo Esaki
'for his experimental discoveries regarding tunneling phenomena in semiconductors'

1985
Klaus von Klitzing
'for the discovery of the quantized Hall effect'

[10] www.nobel.se

1998
Robert B. Laughlin
Horst L. Störmer
Daniel C. Tsui
'for their discovery of a new form of quantum fluid with fractionally charged excitations'

2000
Zhores I. Alferov
Herbert Kroemer
'for developing semiconductor heterostructures used in high-speed and opto-electronics'
Jack St. Clair Kilby
'for his part in the invention of the integrated circuit'

2009
Willard S. Boyle
George E. Smith
'for the invention of an imaging semiconductor circuit – the CCD sensor'

2010
Andre Geim
Konstantin Novoselov
'for groundbreaking experiments regarding the two-dimensional material graphene'

1.3 General Information

In Fig. 1.10, the periodic table of elements is shown. In Table 1.1 the physical properties of various semiconductors are summarized.

1909
Karl Ferdinand Braun
(1850–1918)

1914
Max von Laue
(1879–1960)

1915
Sir William Henry Bragg
(1862–1942)

1915
William Laurence Bragg
(1890–1971)

1946
Percy Williams Bridgman
(1882–1961)

1953
William B. Shockley
(1910–1989)

1953
John Bardeen
(1908–1991)

1953
Walter Hauser Brattain
(1902–1987)

1973
Leo Esaki
(*1925)

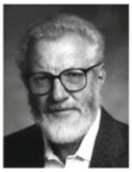
1985
Klaus von Klitzing
(*1943)

1998
Robert B. Laughlin
(*1930)

1998
Horst L. Störmer
(*1949)

1998
Daniel C. Tsui
(*1939)

2000
Zhores I. Alferov
(*1938)



2000
Herbert Kroemer
(*1928)

2000
Jack St. Clair Kilby
(1923–2005)

2009
Willard S. Boyle
(*1924)

2009
George E. Smith
(*1930)

2010
Andre Geim
(*1958)

2010
Konstantin Novoselov
(*1974)

Fig. 1.9. Winners of Nobel Prize in Physics and year of award with great importance for semiconductor physics

Fig. 1.10. Periodic table of elements. From [97]

Table 1.1. Physical properties of various semiconductors at room temperature. 'S' denotes the crystal structure (d: diamond, w: wurtzite, zb: zincblende, ch: chalcopyrite, rs: rocksalt)

	S	a_0 (nm)	E_g (eV)	m_e^*	m_h^*	ϵ_0	n_r	μ_e (cm^2/Vs)	μ_h (cm^2/Vs)
C	d	0.3567	5.45 (Γ)			5.5	2.42	2200	1600
Si	d	0.5431	1.124 (X)	0.98 (m_l) 0.19 (m_t)	0.16 (m_{lh}) 0.5 (m_{hh})	11.7	3.44	1350	480
Ge	d	0.6461	0.67 (L)	1.58 (m_l) 0.08 (m_t)	0.04 (m_{lh}) 0.3 (m_{hh})	16.3	4.00	3900	1900
α-Sn	d	0.64892	0.08 (Γ)	0.02				2000	1000
3C-SiC	zb	0.436	2.4			9.7	2.7	1000	50
4H-SiC	w	0.3073 (a) 1.005 (c)	3.26			9.6	2.7		120
6H-SiC	w	0.30806 (a) 1.5117 (c)	3.101			10.2	2.7	1140	850
AlN	w	0.3111 (a) 0.4978 (c)	6.2			8.5	3.32		
AlP	zb	0.54625	2.43 (X)	0.13		9.8	3.0	80	
AlAs	zb	0.56605	2.16 (X)	0.5	0.49 (m_{lh}) 1.06 (m_{hh})	12		1000	80
AlSb	zb	0.61335	1.52 X)	0.11	0.39	11	3.4	200	300
GaN	w	0.3189 (a) 0.5185 (c)	3.4 (Γ)	0.2	0.8	12	2.4	1500	

Table 1.1. (continued)

	S	a_0 (nm)	E_g (eV)	m_e^*	m_h^*	ϵ_0	n_r	μ_e (cm^2/Vs)	μ_h (cm^2/Vs)
GaP	zb	0.54506	2.26 (Γ)	0.13	0.67	10	3.37	300	150
GaAs	zb	0.56533	1.42 (Γ)	0.067	0.12 (m_{lh}) 0.5 (m_{hh})	12.5	3.4	8500	400
GaSb	zb	0.60954	0.72 (Γ)	0.045	0.39	15	3.9	5000	1000
InN	w	0.3533 (a) 0.5693 (c)	0.9 (Γ)						
InP	zb	0.58686	1.35 (Γ)	0.07	0.4	12.1	3.37	4000	600
InAs	zb	0.60584	0.36 (Γ)	0.028	0.33	12.5	3.42	22 600	200
InSb	zb	0.64788	0.18 (Γ)	0.013	0.18	18	3.75	100 000	1700
ZnO	w	0.325 (a) 0.5206 (c)	3.4 (Γ)	0.24	0.59	6.5	2.2	220	
ZnS	zb	0.54109	3.6 (Γ)	0.3		8.3	2.4	110	
ZnSe	zb	0.56686	2.58 (Γ)	0.17		8.1	2.89	600	
ZnTe	zb	0.61037	2.25 (Γ)	0.15		9.7	3.56		
CdO	rs	0.47	2.16						
CdS	w	0.416 (a) 0.6756 (c)	2.42 (Γ)	0.2	0.7	8.9	2.5	250	
CdSe	zb	0.650	1.73 (Γ)	0.13	0.4	10.6		650	
CdTe	zb	0.64816	1.50 (Γ)	0.11	0.35	10.9	2.75	1050	100

Table 1.1. (continued)

	S	a_0 (nm)	E_g (eV)	m_e^*	m_h^*	ϵ_0	n_r	μ_e (cm^2/Vs)	μ_h (cm^2/Vs)
MgO	rs	0.421	7.3						
HgS	zb	0.5852	2.0 (Γ)					50	
HgSe	zb	0.6084	−0.15 (Γ)	0.045		25		18 500	
HgTe	zb	0.64616	−0.15 (Γ)	0.029	0.3	20	3.7	22 000	100
PbS	rs	0.5936	0.37 (L)	0.1	0.1	170	3.7	500	600
PbSe	rs	0.6147	0.26 (L)	0.07 (m_{lh}) 0.039 (m_{hh})	0.06 (m_{lh}) 0.03 (m_{hh})	250		1800	930
PbTe	rs	0.645	0.29 (L)	0.24 (m_{lh}) 0.02 (m_{hh})	0.3 (m_{lh}) 0.02 (m_{hh})	412		1400	1100
$ZnSiP_2$	ch	0.54 (a) 1.0441 (c)	2.96 (Γ)	0.07					
$ZnGeP_2$	ch	0.5465 (a) 1.0771 (c)	2.34 (Γ)		0.5				
$ZnSnP_2$	ch	0.5651 (a) 1.1302 (c)	1.66 (Γ)						
$CuInS_2$	ch	0.523 (a) 1.113 (c)	1.53 (Γ)						
$CuGaS_2$	ch	0.5347 (a) 1.0474 (c)	2.5 (Γ)						
$CuInSe_2$	ch	0.5784 (a) 1.162 (c)	1.0 (Γ)						
$CuGaSe_2$	ch	0.5614 (a) 1.103 (c)	1.7 (Γ)						