Physica C 514 (2015) 36–45

Contents lists available at ScienceDirect

Physica C

journal homepage: www.elsevier.com/locate/physc

Superconductivity in doped semiconductors

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ARTICLE INFO

Article history:
Received 2 December 2014
Received in revised form 16 January 2015
Accepted 15 February 2015
Available online 24 February 2015

Keywords:
Superconductivity
Degenerate semiconductors

ABSTRACT

A historical survey of the main normal and superconducting state properties of several semiconductors doped into superconductivity is proposed. This class of materials includes selenides, tellurides, oxides and column-IV semiconductors. Most of the experimental data point to a weak coupling pairing mechanism, probably phonon-mediated in the case of diamond, but probably not in the case of strontium titanate, these being the most intensively studied materials over the last decade. Despite promising theoretical predictions based on a conventional mechanism, the occurrence of critical temperatures significantly higher than 10 K has not been yet verified. However, the class provides an enticing playground for testing theories and devices alike.

Contents

1. Introduction: half a century in a nutshell

The notion that "doping" an insulating material by inserting or substituting atoms with a different valence state may bring about superconductivity (below an experimentally accessible critical temperature T_C) is not new. It has been successfully applied to various classes of solids, whereby the resulting free carrier density became a tunable variable, as illustrated in many contributions to this special issue. However, there was a time when the occurrence of superconductivity in materials with appreciably less than one carrier per atom was an open question. The main reason for this was that a lower carrier density was expected to reduce the efficiency of dielectric screening to the point where Coulomb repulsion could not be overcome by any pairing mechanism. In this context, the idea that semiconductors chemically doped beyond the critical value n_{MIT} for a metal–insulator transition to occur would eventually become superconductors was suggested and discussed quite early on for three-dimensional (3d) degenerate systems [1–4]. It was experimentally applied in the 60s to self-doped (with holes) narrow bandgap semiconductors, mostly tellurides such as GeTe [5,6], SnTe [7–9], and the at that time more controversial PbTe [10,11]. Electron doped systems were also investigated such as $La_{3-y}Se_4$ [12,13] and other lanthanum compounds, or the more popular reduced (or Nb-doped) $SrTiO_3$ [14,15], a much wider bandgap semiconductor. In the case of GeTe, the "gap ratio" of the superconducting gap width 2Δ (Δ being the binding energy of the Cooper pair) to its critical thermal energy k_BT_C was measured [16]. The value of 4.3 was taken at the time as a confirmation of the conventional weak coupling mechanism usually referred to as [17] BCS, which predicted a gap ratio of

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http://dx.doi.org/10.1016/j.physc.2015.02.021
0921-4534/

3.5. Probably because increasing the carrier concentration n_e in these systems did not enhance the T_C values above 500 mK (the T_C vs n_e curve even followed a "dome" shape in one case [15], or because the observations remained restricted to "ionic" semiconductors, this initial interest did not last [11,18].

One generation later, the observation of superconductivity (T_C = 8 K) in silicon clathrates where alkaline earth metals had been inserted in the cages for doping showed that sp^3 hybridization of column IV elements was compatible with superconductivity [19,20]. Such experiments were inspired by studies of superconducting alkali-doped fullerenes (see the article by A. Ramirez in this issue). Their quantitative modelling [21] by ab initio calculations and a conventional pairing mechanism illustrated the strength of the electron–phonon coupling in rigid sp^3-bonded networks, and pointed to carbon-based clathrates as a route toward a higher T_C. Although quite telling in hindsight, these findings were not the origin of the discovery published the following year [22] of type II superconductivity (T_C = 2.6 K, onset at 4 K) in polycrystalline boron-doped diamond grown at high pressure and high temperature (HPHT). This seminal report, which included magnetotransport and magnetic susceptibility measurements, was quickly confirmed by other groups for boron-doped polycrystalline [23] and homoepitaxial [24] diamond films grown by Microwave Plasma-enhanced Chemical Vapor Deposition (MPCVD). As reviewed a few years ago [25,26], many groups have reproduced and extended these initial results, with transition onset temperatures soon reaching the 10 K mark in polycrystalline thick films. As for single crystal diamond, the maximum T_C reported so far was 8 K in C:B epilayers [27] grown along (111), written as $C_{(111)}$:B in the following.

Such experimental evidence for superconductivity in boron-doped diamond motivated many theoretical quantitative studies. In order to estimate the maximum critical temperature that could be explained under the assumption of a phonon-assisted pairing mechanism, most of these resorted to numerical calculations involving the Virtual Crystal Approximation [28,29] (VCA), periodic supercells [30,31], or both [32]. In some cases, the random incorporation of boron was taken into account [33–35] by using the Coherent Potential Approximation (CPA). These studies generally used the calculated electronic and vibronic band structure to derive the electron–phonon coupling spectral distribution (the so-called Eliashberg function $\alpha^2F(\omega)$) and to compute the average coupling strength parameter λ by integrating the Ug_F product over the Fermi surface, g_F being the density of electronic states at the Fermi level E_F (defining a Fermi temperature T_F) and U the electron–phonon interaction potential. In diamond, because of the stiff 3d network resulting from sp^3 hybridization of the carbon atoms, U was found to be stronger than in the parent MgB_2 covalent superconductor [36], but g_F was much lower, leading to calculated λ values lying between 0.15 and 0.55 depending on the calculation method, for a doping level in the few at.% range. This was significantly lower than in MgB_2, where λ is close to 1. These theoretical works then used the McMillan formula [37] to estimate T_C as a function of λ, of a logarithmic average phonon frequency represented here by the Debye energy $k_B\theta_D$, and of the screened and retarded Coulomb repulsion potential μ usually expressed as $\mu^* = \mu/[1 + \mu\mathrm{Log}(T_F/\theta_D)]$. With these parameters, this formula reads:

$$T_c = \theta_D/1.45 \exp\left[-(1.04(1+\lambda))/(\lambda - \mu^*(1+0.62\lambda))\right] \quad (1)$$

In diamond, θ_D = 2000 K, quite a high value. As for μ^*, most of the authors assumed that the values typical for metals (μ^* = 0.15) still applied, despite the fact that the Fermi energy E_F and the average phonon energy described by $k_B\theta_D$ were comparable in superconducting diamond (see Table 1). Such an approach reproduced most of the trends of the experimental results, such as the magnitude of T_C or the negative sign of the pressure coefficient [38], and provided some insight as to which phonons contributed most significantly to the coupling [30–32]. However, the simulations failed to reproduce the values of T_C when the free hole concentration n_h was reduced down to n_{MIT}, as well as the curvature of the experimental T_C vs n_h variations [34,35,39,40]. Rescaling the coupling and screening parameters λ and μ^* according to power laws close to the critical concentration has been proposed for diamond [40] and silicon [41] but remains specific and unsatisfactory. More general descriptions [42,43] of the effect of approaching the MIT in disordered metals yield T_C enhancements which have not been detected in the materials under study here. Unfortunately, the powerful parameter-free approach where the Coulomb pseudo-potential μ does not need to be adjusted [44] has not been applied to any of the superconducting semiconductors so far. This situation prompted alternative theoretical approaches either based on the resonating valence bond model which assumes transport within an impurity band [45], at the crossover between the host band and the impurity band [46], or which relied on attractive spin–spin interactions between weakly localized holes near the Fermi level [47,48]. Meanwhile, under the assumption of optical phonon-mediated pairing, the maximum achievable T_C in diamond has been tentatively estimated [49,50]. In a similar manner, it was predicted [51,52] that the rhombohedral $B_{13}C_2$ and cubic BC_5 compounds would yield a T_C value close to that observed in MgB_2.

The calculated transition temperatures of a few *K* as detailed above for hole-doped diamond were also considered by some authors [28,53] to be in sufficient agreement with experiment to warrant predictions of p-type superconductivity in other column IV semiconducting materials, namely Si and Ge. Despite the notorious incapacity of BCS theory to predict new superconductors [54], experimental evidence for superconductivity was gathered over the next few years, first in silicon [55], then in silicon carbide [56], both upon boron doping in the few at.% range, with T_C soon [57] reaching 1.5 K in 3C–SiC:B and 6H–SiC:B (cubic 3C and hexagonal 6H are two of the many polytypes of silicon carbide), and more recently [41] 0.7 K in Si:B. Ab initio calculations in the spirit

Table 1
Normal state general properties of some superconducting semiconductors. The bandgap width E_G, the Debye temperature θ_D and the relative permittivity at low frequency ε_r are those of the undoped material. The minimum carrier concentration for which superconductivity has been reported ($n_C$min) has been measured by Hall effect, except for silicon (italics). The Fermi temperature T_F was estimated by assuming an effective mass m^* = 1.

	Low *T* crystal phase	E_G (eV)	θ_D (K)	ε_r ($/\varepsilon_0$)	Dop.	r_{Bohr} (nm)	$n_C$min (nm^{-3})	$T_F$min (K)
SnTe	Rocksalt	0.19–0.3	140	1200	V_{Sn}	230	0.25 [98]	1680
GeTe	fcr distorted	0.1–0.2	170	36	V_{Ge}	2	0.9 [98]	3950
PbTe	Rocksalt	0.35	140	1000	Tl, In	250	0.05	570
$SrTiO_3$ n-type	Tetragonal (perovskite)	3.1	450	20000	V_O, Nb	600	0.0005 [94]	24 [94]
Ge	Diamond	0.66	360	16	Ga	5	0.2 [67]	1450
Si	Diamond	1.1	640	12	B	2	*0.3* [41]	1890
3C–SiC	Zincblende	2.4	1270	9.7	B, Al	1	0.4 [62]	2300
6H–SiC	Hexagonal	3	1200	9.6–10	B	1	0.25 [57]	1680
C	Diamond	5.5	2000	5.7	B	0.4	0.4 [27]	2300