Non-Crystalline Chalcogenides

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Aims and Scope of the Series

The aim of this series is to present monographs on semiconductor materials processing and device technology, discussing theory formation and experimental characterization of solid-state devices in relation to their application in electronic systems, their manufacturing, their reliability, and their limitations (fundamental or technology dependent). This area is highly interdisciplinary and embraces the cross-section of physics of condensed matter, materials science and electrical engineering.

Undisputedly during the second half of this century world society is rapidly changing owing to the revolutionary impact of new solid-state based concepts. Underlying this spectacular product development is a steady progress in solid-state electronics, an area of applied physics exploiting basic physical concepts established during the first half of this century. Since their invention, transistors of various types and their corresponding integrated circuits (ICs) have been widely exploited covering progress in such areas as microminiaturization, megabit complexity, gigabit speed, accurate data conversion and/or high power applications. In addition, a growing number of devices are being developed exploiting the interaction between electrons and radiation, heat, pressure, etc., preferably by merging with ICs.

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The texts will be of a level suitable for graduate students, researchers in the above fields, practitioners, engineers, consultants, etc., with an emphasis on readability, clarity, relevance and applicability.

The titles published in this series are listed at the end of this volume.

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INTRODUCTION

The earliest experimental data on an oxygen-free glass have been published by Schulz-Sellack in 1870 [1]. Later on, in 1902, Wood [2], as well as Meier in 1910 [3], carried out the first researches on the optical properties of vitreous selenium.

The interest in the glasses that exhibit transparency in the infrared region of the optical spectrum rose at the beginning of the twentieth century. Firstly were investigated the heavy metal oxides and the transparency limit was extended from 3 ÷5 μm (the case of the classical oxide glasses) up to 7 ÷ 8 μm wavelength. In order to extend this limit above 8 μm, the scientists tried the chemical compositions based on the elements of the sixth group of the Periodic Table, the chalcogens: sulphur, selenium and tellurium.

The systematic research in the field of glasses based on chalcogens, called chalcogenide glasses, started at the middle of our century. In 1950 Frerichs [4] investigated the As_2S_3 glass and published the paper: "New optical glasses transparent in infrared up to 12 μm". Several years later he started the study of the selenium glass and prepared several binary glasses with sulphur [5]. Glaze and co-workers [6] developed in 1957 the first method for the preparation of the As_2S_3 glass at the industrial scale, while Winter-Klein [7] published reports on numerous chalcogenides prepared in the vitreous state.

As compared to the oxide glasses, the mechanical strength and the thermal stability of the chalcogenide glasses are significantly lower, while the thermal expansion coefficient and the temperature coefficient of the refractive index are higher. The range of infrared transparency, controlled by higher atom masses and lower bonding force constants in the chalcogenide combinations is essentially broadened towards higher wavelengths (lower wave numbers).

The decrease of the average bonding energy in solids, which is related to the increase of the mass of the atoms in the homologous rows of the Periodic Table has as a consequence the narrowing of the hole band in their electronic band structure. By thermal activation of the charge carriers a not too high electrical conductivity is obtained. Many glasses are known, which exhibit an electrical conductivity of $\sigma \sim 10^{3} \div 10^{-1}\ \Omega^{-1}cm^{-1}$ at 298 K.

The chalcogenide glasses are situated close to the oxide glasses with electronic conduction and form a new group of glasses with semiconducting properties.

The first research program in the field of chalcogenide glasses was initiated in 1955 by two competing groups of physicists and chemists from Sankt-Petersburg: the group from "A.F. Joffe" Physico-Technical Institute, led by B.T. Kolomiets and N.A. Goryunova, who discovered the first semiconducting glass, $TlAsSe_2$ [8], in the system $Tl_2Se{\cdot}Sb_2Se_3$-$Tl_2Se{\cdot}As_2Se_3$, and the group from the University of Sankt-Petersburg (former Leningrad University) led Prof. R.L. Myuller [9]. Later, in 1968, S.R. Ovshinsky and his co-workers [10] from Energy Conversion Devices (Troy, Michigan, USA),

discovered the memory and switching effects exhibited by some chalcogenide glasses. The unusual electrical effects in chalcogenides stimulated the development of the theory and applications of chalcogenide materials. From that time, new phenomena, properties and effects have been discovered in the non-crystalline chalcogenides. In parallel, the chalcogenides have been applied in xerography, holography, computer memories, radiometry and optical transmission of the information. The recent discovery of induced and of stable anisotropy, as well as the discovery of the optical non-linear properties of several chalcogenide materials, opened new horizons for optoelectronic applications.

Although the work in the field of non-crystalline chalcogenides, along more than forty years, resulted in a huge amount of theoretical and experimental results, there are few reviews and books aiming to cover both the scientific and technological aspects of these advanced materials.

A comprehensive work on the theory and properties of the non-crystalline materials including the chalcogenide ones has been published in 1971 by Sir N.F. Mott (Nobel Prize Winner for Physics, 1977) and E.A. Davis ("Electronic Processes in the Non-Crystalline Materials", Oxford University Press, Second Edition, 1979). A book which includes a chapter related to the chalcogenides was published in 1976 by K.K. Schwarts and co-workers in Soviet Union ("Optical Recording Media"). In the next years, there were published several books that treat the amorphous solids, in general, and the chalcogenide solids in particular: "The Chemistry of Glasses" (1982, A. Paul), "The Physics of Amorphous Solids" (1983, R. Zallen), "Physics of Amorphous Materials" (1983, S.R. Elliott), "Amorphous and Glassy Inorganic Solids" (1983, A. Feltz). The first book entirely dedicated to chalcogenide glasses, entitled "Chalcogenide Semiconducting Glasses", was published in 1983 by Z.U. Borisova, the former co-worker of Prof. R.L. Myuller. One year later, G.Z. Vinogradova, from the Institute for General and Inorganic Chemistry in Moscow published the book: "Glass Formation and Phase Equilibrium in Chalcogenide Systems". In Moldova, Academician A.M. Andriesh and co-workers published in 1988 a book on chalcogenides with special emphasis to applications: "Glassy Semiconductors in Photoelectric Systems for Optical Recording of Information". The book entitled: "The Physics and Applications of Amorphous Semiconductors" published in 1988 by A. Madan and M.P. Shaw in USA is only partly dedicated to chalcogenide glasses. However, a concise and organised textbook on non-crystalline materials and applications is still desired as a valuable resource for graduate students and workers in the field.

The present book aims to give a large, detailed account on the physical and technological aspects of chalcogenide systems including the applications.

The basic information on materials, with special emphasis on preparation, the extent of the glassy domain and the crystal-chemistry of chalcogenides, is covered in chapter 1.

The general physico-chemical properties of the chalcogenide glasses with a special look on the chalcogens and binary glasses are discussed in chapter 2.

The most important properties of the chalcogenide glasses are those related to the effects induced by various external factors, in particular light and other radiations. These effects are of great interest in applications and are treated in detail, both from experimental and theoretical point of view, in chapter 3.

Finally, chapter 4 is dedicated to applications, a continuously expanding field.

The topics include the author's original works as well as his recent results, some of them not yet published, on the structure and properties of non-crystalline chalcogenide materials.

The book is intended for use as a reference and research book for graduate students, scientists and engineers working in the field of materials science and device physics.

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THE CHALCOGENS AND THEIR COMBINATIONS

1.1. The Chalcogens

The chalcogen elements belong to the VI-A subgroup of the Periodic Table. These elements are: sulphur, selenium and tellurium. The VI-A subgroup contains also the oxygen and polonium. The chalcogens are the basic elements of the chalcogenides compounds. The chalcogenides are compounds of sulphur, selenium or tellurium with electropositive elements or with organic radicals. The name chalcogenide originates from Greek: χαλκοζ=copper, γενναω=born and ειδοζ=type being given initially to the chalcogenide minerals that contain copper in combination with sulphur, selenium and tellurium.

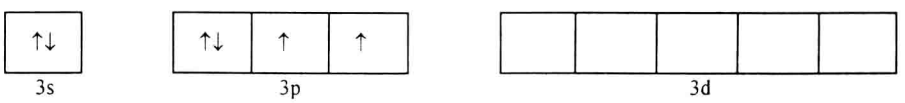
1.1.1. SULPHUR (S)

Sulphur was known from the old times of the humanity. Four thousand years ago Homer mentioned this element and later the Bible described "its power". For many centuries, sulphur was used for paintings, for whitening the linen, in cosmetics and medicine (about 1600 year b.C.). Berzelius discovered sulphur as chemical element in 1817. In 1822, Mitcherlich discovered the allotropy of sulphur.

Sulphur has the order number Z=16 and its atomic mass is 32.064. On the scale of natural abundance, sulphur is situated at the position 15. In the Earth core the sulphur concentration is 5×10^{-2} at. % and in the planetary ocean is 9×10^{-2} at. %. The sulphur appears both as native element and in the compounds as e.g.: sulphides (Sb_2S_3 - antimonite, Ag_2S - argentite, FeAsS - arsenopyrite, PbS - galena, CoAsS - cobaltine, HgS - cinnabar, FeS_2 - pyrite, $CuFeS_2$ - chalcopyrite, ZnS - würtzite or zinc blende, etc.). Much sulphur can be found in carbon, bituminous schist, oil, thermal springs and volcanic gases.

The natural sulphur contains four stable isotopes: $^{32}S(95.02\%)$,$^{33}S(0.75\%)$, $^{34}S(4.21\%)$ and $^{36}S(0.02\%)$.

The valence electronic shell of sulphur has 6 electrons with the disposal $3s^23p^4$:



The sulphur, can be found in the following oxidation states: -2, 0, +2, +3, +4, +5, +6. It is a typical non-metal. The maximum co-ordination number of sulphur is 6 and the most stable state is the hybrid state sp^3.

The sulphur exhibits several crystalline and non-crystalline forms. In order to explain the atomic scale structure in the solid and liquid phase we must to take into account some peculiarities of the chemical bonding.

Sulphur forms di-covalent bonds. It has two unpaired p electrons and can form σ-type bonds. The p orbitals are oriented reciprocally at 90° angles. The angle between sulphur bonds is 105°. This value is very near to the characteristic angle for the sp^3 hybridisation. Starting from these bonds it is possible to define two distinct positions in the series of four bonded atoms: the cis or eclipsed position and the trans or staggered position (figure 1.1)

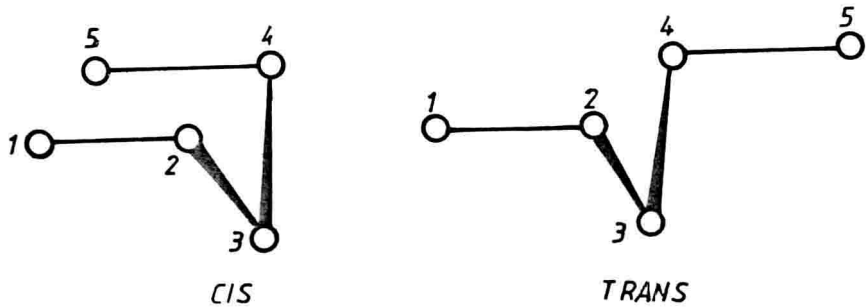


Figure 1.1. The eclipsed (cis) and staggered (trans) configuration of the chalcogen bonds.

The bonding in the configuration cis leads to the formation of ring molecules (S_6, S_8...) and the bonding in the configuration trans leads to the formation of chain-like molecules. The angles between the planes defined by the atoms of a given configuration are called dihedral angles. These angles are situated in the interval 90-100°. If only σ-bonds should exist then a random rotation angle around a common bond should be expected. The special situation of two types of configurations appears due to the contribution of the π-bonds between the p-electron pairs on neighbouring atoms. The ring (crown) molecules S_8 give the most stable structural configuration in the solid state. Other molecules as e.g. S_6, S_4 and also long chains of atoms (S_∞) can be packed in the solid state of sulphur.

The Crystalline Forms of Sulphur

A. Orthorhombic S (S_α). The orthorhombic structure of sulphur is stable up to the temperature of 95.6 °C. The space group is D_{2h}^{24}-F_{ddd} and the unit cell contains 128 atoms configured in 8-fold rings (Figure 1.2). In the rings the atoms exhibit the trans configuration with the dihedral angles of 102°. The bond angle is 105°. The lattice parameters were determined with highest accuracy by Cooper et al. [1] at 24.8 °C:
a = (10.4646 ± 0.0001) Å, b = (12.8660 ± 0.0001) Å; c = (24.4860 ± 0.0003) Å; β = 107°48' ± 25'. The average distance between two bonded sulphur atoms is (2.048 ± 0.002) Å.

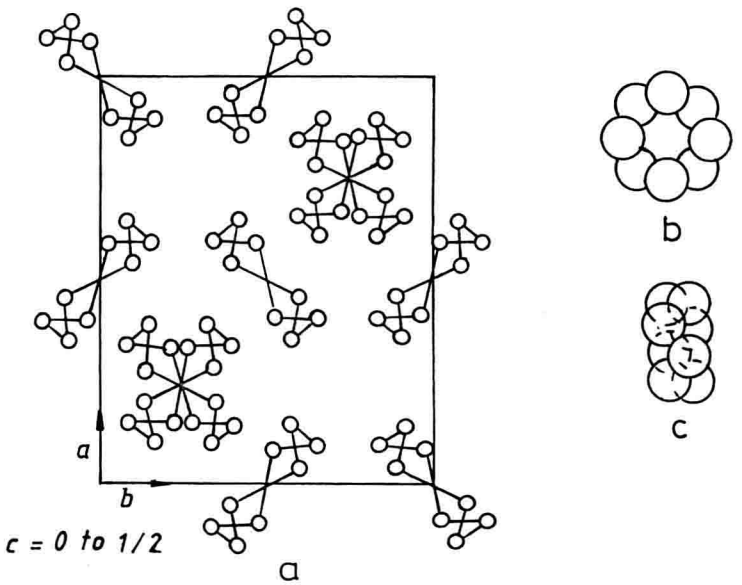


Figure 1.2. The unit cell of the orthorhombic sulphur (S_α).
a. the ring packing b. c. front view and side view of the S_8 ring.

B. Monoclinic Sulphur (S_β). The orthorhombic sulphur transforms enantiomorphically and irreversibly in monoclinic sulphur at 95.6 °C and is stable up to the melting point (119.25 °C). The transformation takes place only under slow heating regime. The space group of the monoclinic sulphur is C_{2h}^5-$P2_1/b$ and the unit cell contains six 8-fold rings. The lattice parameters have been determined by Burwell [2] at the temperature of 103 °C: a = 10.90 Å; b = 10.96 Å; c = 11.02 Å; β=83°16'.

C. Rhombohedral Sulphur (S_ρ or S_ε). The rhombohedral modification of sulphur has been reported as early as 1891 by Engel [3]. The rhombohedral sulphur is unstable at room temperature and transforms into plastic sulphur, which gradually changes into the orthorhombic sulphur.

The rhombohedral sulphur can be obtained by crystallisation from the saturated solution of sulphur in toluene. The probable space group is C_{3i}^2-R_3 and the unit cell contains 36 sulphur atoms grouped in six-fold rings. The lattice parameters are: a = 6.45 Å; α = 115°8' [4] or a = 10.818 Å and c = 4.280 Å in the hexagonal reference frame [5]. The length of the sulphur-sulphur bond is 2.0 Å and S-S-S bond angles are around 100°. In the six-fold sulphur rings the bond angles are 104° and the dihedral angles are 71° (Fig. 1.3).

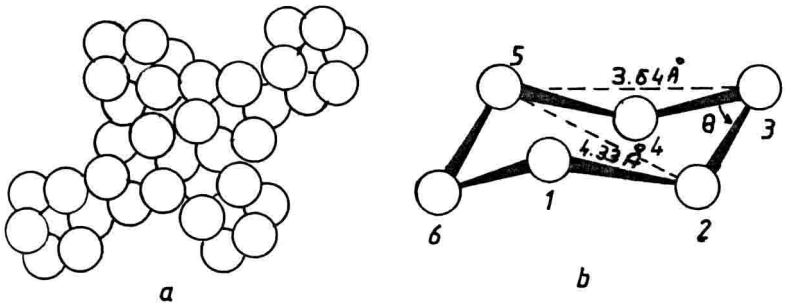


Figure 1.3. The packing of the sulphur atoms in the unit cell of the rhombohedral structure. (The picture is valid, also, for rhombohedral selenium).
a. View of the S_6 ring packing along the [001] axis.
b. The six-fold ring (the distances are for selenium).

D. γ-Sulphur (S_γ). This is a special monoclinic structure obtained by crystallisation of sulphur dissolved in some solvents (e.g. in alcohols). The crystallites are needle-like. S_γ is metastable and slowly transforms into orthorhombic sulphur. The space group of S_γ is C_{2h}^1 - $P_{2/m}$. The unit cell contains 32 atoms grouped in four 8-fold rings (Fig. 1.4). The lattice parameters are [6]: a = 8.57 Å; b = 13.05 Å: c = 8.23 Å; ß = 112° 54'.

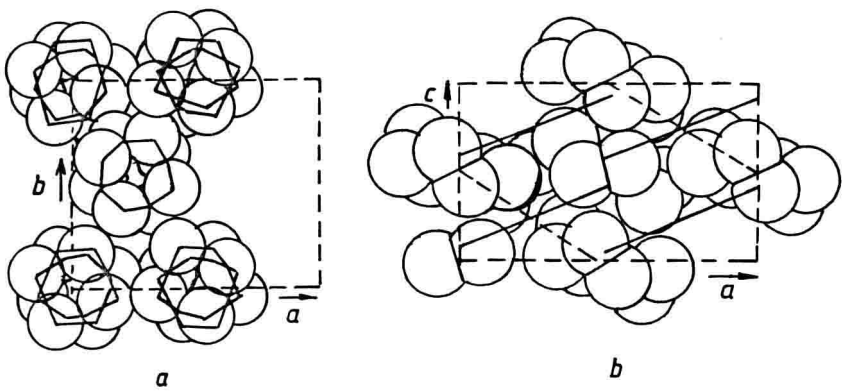


Figure 1.4. The unit cell of the monoclinic γ-sulphur.
The packing of the S_8 rings viewed: a. along the axis c b. along the axis b.

E. Orthorhombic Sulphur (S'_α). This form of sulphur has been discovered in 1966 [7] in the powder obtained during the reaction of S_xCl_2 and H_2S_y (x+y=12) and up to day no complete structural studies have been conducted. There were reported orthorhombic crystals with a = 4.730 Å, b = 9.104 Å, c = 14.574 Å. It seems that this unstable form contains two 12-fold sulphur rings in the unit cell.

F. Fibrous Sulphur (S_{φ}). The fibrous sulphur is obtained by the application of a stretching force to the plastic, non-crystalline sulphur. The space group seems to be C_{2v}^{12} [8].

The monoclinic cell contains 112 atoms and the lattice parameters are: a=26.4 Å; b=9.26 Å; c=12.32 Å; β=79°15'. The density is 2.01 g/cm^3. It is supposed that the fibrous sulphur is in fact a superposition of two forms of sulphur: one soluble form would be S_γ and the other one would be the so-called sulphur ψ(S_ψ) which consists from helical micelles with the periodicity of 10 sulphur atoms for 3 complete turns [9]. Sulphur ψ is characterised by a dihedral angle of 85° and a bond angle of 106° [10]. The fibrous sulphur transforms slowly into the orthorhombic S_α sulphur. The total number of allotropes of sulphur reported in literature is close to 50 but very few of them have been satisfactorily characterised. An excellent review of these allotropes is given in [11,12].

The Amorphous States of Sulphur

During quenching the orthorhombic sulphur S_α does not succeed to transform into monoclinic sulphur and melts at 112.8 °C as a viscous yellow liquid called sulphur λ (S_λ) or cycle-octasulphur. The liquid sulphur exhibits an anomalous dependency on temperature of the viscosity. By heating the liquid, its viscosity firstly decreases (down to 6.5×10^{-3} poise*s at 155 °C), further increases and then the liquid colour becomes dark-brown. At about 187 °C the sulphur viscosity reaches 93.3 poise's and, thereafter, gradually decreases so that at 300 °C the sulphur becomes again a soft, fluid mass. The liquid sulphur boils at 444.60 °C and its viscosity at the boiling temperature reaches 8.3×10^{-2} poise*s. These phenomena can be explained by the dissociation of the sulphur molecules in the melt and the competitive recombination of the atoms. This lead to an equilibrium for the concentration of various kinds of rings. The fraction of S_8 rings is 90% mol., as deduced from the decrease of the melting point of the monoclinic sulphur by slow heating. The rest of the melt consists in 6-fold rings and other bigger cyclic molecules up to S_{30}. The macromolecule rings do not appear at low temperatures due to sulphur tendency to be bonded in cis (eclipsed) configuration. Nevertheless, when the temperature is raised, the probability for the bonding in trans configuration increases and at the critical temperature of 160°C this configuration becomes dominant. As a consequence, the viscosity of the melt strongly increases and this leads to the parallel orientation of the molecules. This orientation favours the formation of long, closed chains in equilibrium with the small rings. At high temperatures the sulphur melt contains only about 40% small molecular rings. The remnant part consists mainly in very large macromolecule rings (up to 5000 atoms).

It was definitely established that liquid sulphur contains three main components: λ-sulphur, μ-sulphur and π-sulphur. When the liquid sulphur is further heated the S_μ content increases. The S_μ viscosity is higher than that of S_λ because by heating the liquid becomes viscous. The S_π component is at variance with the S_μ component as concerning the rate of dissolution in CS_2. S_π transforms spontaneously in S_μ. The following equilibrium equation can be written:

$$S_\lambda \leftrightarrow S_\mu + S_\pi \qquad (1.1)$$

The researches have shown that both S_λ and S_μ are based mainly on S_8 ring configurations while S_μ contains long chains. S_π would contain, additionally, a few sixfold rings, which explain the difference in solubility between S_π and S_μ . The S_8 rings open at ~ 160 C.

The analysis of the radial distribution curves indicated that in liquid and amorphous sulphur the S_8 molecules exhibit a tendency towards ordering based on lattice fragments with orthorhombic structure. The S_8 molecules interact by weak chemical bonds [13]. It is quite remarkable that both sulphur rings and chains play an important role for the amorphous state. The rings act as plastifiers in the process of stretching the amorphous plastic sulphur. Moreover, they prevent the closer approaching of the chains one to another. On the other hand the chains prevent the approaching and the ordering of the sulphur rings. Thus the amorphous, disordered state is stabilised.

1.1.2. SELENIUM (Se)

Selenium is the element with Z=34 in the Periodic Table, and its atomic mass is 78.96. In the Earth shell its abundance is 8×10^{-5} at.%. The native selenium is very rare. Usually, selenium is found in sulphide minerals (more than 40 minerals), for example: $FeSe_2$, $NiSe_2$, $CoSe_2$, CuSe, ZnSe, Fe_3CuSe4, HgSe, $As_2(S,Se)_2$, Bi_2Se_3, PbSe, Ag_2Se, CdSe, Ag_4SeS, $PbSeO_4$, etc..

The natural selenium consists of 6 stable isotopes: ^{74} Se (0.98 %); ^{76}Se(9.02 %); ^{77}Se (7.58 %); ^{78}Se (23.52 %); ^{80}Se (49.82 %); ^{82}Se (9.19 %).

The configuration of the valence electrons of selenium is $4s^24p^4$. The oxidation states of selenium are -2; 0; +2; +4; +6. The sp^3 hybridisation is less stable than in sulphur.

The Crystalline States of Selenium

The particular features of the crystalline states of selenium are based on the tendency of the selenium atom to have the trans configuration more expressed than sulphur atom. All the crystalline forms of selenium show configurations with two first order neighbours situated at distances between 2.32 Å and 2.40 Å.

A. Hexagonal (grey or metallic) Selenium (Se_γ). This is the most stable form of selenium. The lattice is made from parallel helical chains (Fig. 1.5). Every atom has two neighbours in its own chain situated at 2.30÷2.37 Å and four neighbours situated in neighbouring chains at 3.42 Å÷3.48 Å. The radius of the helix is 0.984 Å. Within the selenium chains the atoms are bonded by covalent bonds and between chains act molecular forces of the Van der Waals type with a weak metallic component. The hexagonal unit cell contains three atoms. The lattice parameters measured at the temperature of 18 °C are [14,15]: a = 4.3544 Å, c = 4.9496 Å, c/a = 1.1367. The bond angle is 103.1 ± 0.2 ° and the torsion (dihedral) angle is 100.7 ± 0.1°.