APPLICATION OF SOME COMPUTATIONAL METHODS IN STUDYING THE X-RAY DIFFRACTION STRUCTURE OF SOME AMORPHOUS COMPOUNDS

A THESIS

Submitted in Partial Fulfillment for the Requirements of the
MASTER DEGREE OF SCIENCE
(in Physics)

By

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(B. Sc. of Physics)

To
Faculty of Science
Ain Shams University
Cairo, Egypt

1987

ACKNOWLEDGMENT

The author wishes to record his deep appreciation and gratitude to Prof. Dr. Karimat El-Sayed, Ain Shams University, Faculty of Science, Physics Department, for suggesting the field of present research, valuable guidance and fruitful discussions.

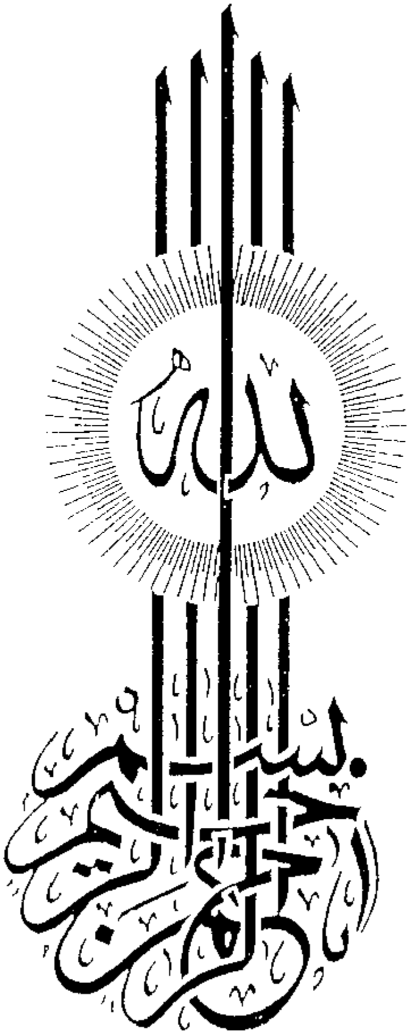
Thanks are due to Prof. Dr. A.H. Moussa, Head of Physics Department, Faculty of Science, Ain Shams University for the departmental facilities rendered.

Deep thanks are due to Dr. Abd El-Rahman M. Abd El-Rahman for his continuous guidance and fruitful introduced ideas in this work.

Great thanks are due to Dr. A.M. Salem, the Director of the Computer Center for his computer facilities and valuable cooperations.

Finally, the author would like warmly to express his sincere gratitude to the group members of X-ray group and other collaborators in Physics Department, Faculty of Science, Ain Shams University.

A.A.A. Shama
January 1987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SUMMARY

This work is divided into two parts, the first part deals with implementing a computer program called RADILS which is specially designed for finding the structure of amorphous materials and alloys from X-ray diffraction data, (this program can also be applied to electron and neutron diffraction data).

The second part deals with applying the implemented program to find the structure of amorphous Ge. In the first part the program was highly adapted and implemented with great efficiency on the local computer installed in Ain Shams University. The silica glass was the test sample used in the program. After making the necessary alterations in the program and running it on the local computer on the test sample, the test sample gave structure data in good comparison with the original ones, which indicates a good implementation of the program with high efficiency.

In the second part the implemented program was used to investigate the structure of amorphous germanium. The structure was investigated through finding the most suitable theoretical model which can fits the experimental data.

Several models were proposed, namely Diamond struture model Tetragonal structure model, and finally Wurtzite model, but none of these models fit perfectly well the experimental results. The Diamond structure was the nearest to the experimental fit, but not perfectly well. The other two structures

were far away from the structural configuration of the amorphous germanium. As a result of this finding the structural model which was suggested to describe accurately well the structure of amorphous Ge was what is called a "regional distorted diamond model". This distortion was revealed by electron microscopy examination when trying to study the process of crystallization of Ge in situ under the vacuum of the electron microscope. This investigation revealed the presence of small percentage of tetragonal crystals in the main bulk of the cubic crystals. This may confirm the hypothesis of the regional distorted Diamond structure model for the structure of the amorphous Ge.

CHAPTER I

INTRODUCTION

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The semiconductors silicon and germanium crystallize in the diamond structure. Some authors may classify these two materials as semimetal elements, but the diamond structure and their energy gap values, (in germanium is ~0.71 eV, and in silicon is ~1.1 eV), may reveal their properties as semiconducting elements. Each atom in these materials is surrounded by four like neighbours, and the four outer electrons of each atom form electron-pair, (or covalent), bonds with each neighbour (Aldert Vander ziel, 1971)(1). In technology Ge and Si was applied in transistors manufacturing as a three terminal electronic device for their interesting electronic properties. Recently when thin film technique was advanced and used in preparing solar cell, Ge was used in constructing such cell. In this technique a pentavelent element is deposited at first as a donor substrate (n-type Ge element), on which a p-type Ge is evaporated as a thin film (~ thickness of Angestroms) to form a p-n junction of germanium which has characteristic features, such a system is one type of "a solar cell".

In a parallel way when germanium and silicon are prepared as amorphous samples they display another interesting electronic properties such as switching and memory effects (Ovshinsky, 1968, 1969)(2,3). From an engineering point of view, amorphous semiconductors are closer to practical usage for electronic devices than metallic glasses. This situation has stimulated the investigation of these materials, and thus good progress has been made on amorphous semiconductors that have been reviewed in texts (Alder, 1971, Le Comber and Mort, 1973)(4,5).

1.1- Early Work On Amorphous Germanium :

Great amount of experimental and theoretical investigation have been done in order to reveal the structure of amorphous Ge and Si. The definitive work on amorphous Si was done by Moss and Graczyk, 1969, 1970(6,7). Using electron diffraction techniques they determined the electron scattering from thin film of amorphous Si. From large angle scattering they calculated the electron diffraction function and by performing a Fourier transform they deduced the radial distribution function (RDF) of the material. In addition from small angle scattering they concluded that amorphous Si as deposited contains voids or regions of low density which may be annealed by heating. Shevchik and Paul in 1972(8), using X-ray diffraction have presented similar data for amorphous Ge films produced by sputtering, evaporation, and electrodeposition. In both works they showed that the radial distribution functions (RDF's) of amorphous Ge and Si are essentially identical (except that the Ge-Ge bond length is ≈ 4% larger than that of Si-Si, just as that in the crystalline state). In addition the diffraction functions for the two materials also agree extremely well except that the reduced data for

Si tend to zero faster than those of Ge, at large scattering angles.

The interesting features of amorphous Ge have activated many workers to determine its structure as a key point for knowing the differences in structure of semiconductor materials. And accordingly, many workers have constructed their theoretical model to be satisfied by their obtained experimental results. "A network model" was suggested by Polk in 1971(9). In a restrained manner the continuous random network (CRN) (may be applied in case of small angle scattering) was also suggested by Polk in 1971(9). As a consequential way a computer simulation method was suggested by Shevchik in 1972(10). The second experimental approach was suggested by Rudee, Howie and Coworkers (1972, 1973)(11,12), they employed high resolution techniques of electron microscopy to study amorphous Ge directly. Their results could not be explained by the random network model, and they suggested that the structure of amorphous Ge can best be represented by a micro-crystallite model, with a crystallite diameter of ~14 Å. Weinstein in 1973(13) has shown later that the micro-crystallite model in its simplest form is inadequate to account for the diffraction data. His results showed that quite acceptable agreement with diffraction data can be obtained using a statistical micro-crystallite model. Grigorivici in 1968(14) reported that it was only by fitting both the radial distribution function and the diffraction function that a good understanding of the structure of amorphous Ge and Si could be attained.

Other workers (1967, 1969)(15,16) in order to explain their experimental RDF's in amorphous Si and Ge adapted the amorphous cluster models. The cluster model is a middle course between the random network and crystallite models.

Recently Rudee et al. in 1972(17) has found an improved fit to his experimental results with the Wurtzite structure. Wurtzite also shows perfect tetrahedral bonding. It has hexagonal symmetry and is composed only of six fold rings. Rudee's success suggested that a calculation of other known tetrahedral crystal structures might give even better fits to the data. It should not be forgotten that several investigators(6,7) have considered the diamond structure to be the normal form in which Ge and Si crystallize but the failure of the diamond structure to account for the experimental RDF's has in large measure been responsible for the dismissal of micro-crystallite models.

Recently Karimat El-Sayed et al. in 1985(18), by using electron microscope have found that on heating in situ the amorphous Ge thin film, two phases of Ge were developed, the normal diamond phase and few percentage of tetragonal crystals.

Two high pressure polytypes of Si and Ge are known as SiIII and GeIII (Wentorf, et al., 1963, Bundy and Kasper, 1963)(19,20). These types have produced great interest currently since they are more disordered than the diamond or Wurtzite structures while maintaining tetrahedral coordination.

Ge also crystallizes in a form such that it has cubic symmetry and is composed of six fold rings but the nearest neighbours occur in eclipsed, staggered and intermediate configurations, (Eclipsed configuration bonding means zero angle of rotation of bonds, while, staggered configuration bonding is the rotation of bonds with respect to each other with sixty degrees), and all the atoms have identical environments, the Ge in this case is known as GeIV (Bates, et al., 1965)(21).

GeIII structure is characterized by quite distorted tetrahedral bonding and has tetragonal symmetry (Kasper, and Richards, 1964)(22). It differs from the previously mentioned structures in two respects :

(i) In addition to six-fold rings, GeIII also has five- and seven-fold rings, which can have important effects on the electronic density of states (Weaire, et al., 1972, Joannopoulos and Cohen, 1973)(23,24).

(ii) There are inequivalent types of atoms in GeIII, that is to say, two different arrangements of neighbours. For this reason GeIII presents a crystalline structure which has many of the features of an amorphous material.

Other crystal structures considered were suggested by the work of Grigorivici in 1968(14), who introduced the concept of the "amorphon"-pentagonal dodecahedral unit which is easily formed with minimal distortion of the tetrahedral bonding atoms. In these units, all bonds are eclipsed and only five membered rings are formed.

Finally for completeness, the remaining high pressure polytype of Ge (GeII), the white-tin structure (Wyckoff, 1963)(25) was also considered. The white-tin structure has tetragonal symmetrty. Unlike the other structures mentioned so far, white-tin has distorted tetrahedral coordination with two additional nearest neighbours. The presence of six nearest neighbours has profound effects on the electron diffraction and produces patterns totally unlike the experimental data of the amorphous Ge. For this reason, structures with other than tetrahedral coordination need not be considered further. Table 1, lists these structures, along with their symmetry types, unit cell dimensions, nearest neighbours, nearest neighbour distances and densities.

1.2- Different Models Used for Determining the Structure of Amorphous Materials :

Several models were mentioned before in the early work in order to determine the structure of amorphous Ge. These models are : the network model, the micro-crystallite models and the cluster models. In the past, the network model was applied, but the failure of this model to give agreement between the theory and the experimental results make the exclusion of it more appropriate, in the present discussion. These models are explained in details in the followings :-

(a) The micro-crystallite disorder model :-

In this model many workers support the idea of the short range order (SRO) in amorphous materials which may be strongly

Table 1. "For listing the different type structures of amorphous Ge and crystallographic data used in calculations".
(The bracketed values for Si).

Structure	Crystal symmetry	Space group	Unit cell dimensions in (Å)	No. of atoms per unit cell	Density gm/cc	Nearest neighbour distance in(Å)	$\rho/\rho_{Diamond}$	Reference	Notes
Diamond	Cubic	O_h^7 Fd3m	a= 5.657 (a= 5.431)	8	5.325 (2.33)	2.45 (2.35)	1.000	Wyckoff, (1963)(25)	Theoretical values were chosen to give $\rho/\rho_{Diamond}$ = 1.000
Wurtzite	Hexagonal	D_{6h}^4 $P6_3/mmc$	a=4.00 c=6.53 a=3.84 c=6.27	4	5.325 (2.33)	2.45 (2.35)	1.000	Bundy, and Kasper, (1967)(20)	
GeIII	Tetragonal	D_4^8 $P4_32_12$	a=5.93 c=6.98 a=5.69 c=6.70	12	5.89 (2.58)	2.48 (2.37)	1.106	Kasper, and Richards, (1964)(22)	

related to the crystalline state of these materials, but in the same time the pair correlation functions is only applied through a limited range (or a limited distance) within the system concerned. Fig. 1 represents a schematic diagram of this model.

In this model although small crystallites are disorderly distributed, the inhomogenity of the atomic configuration in the boundary region is not considered. More developments have been made in order to make the micro-crystallite model fit the experimental results and this by beginning with larger local units having a desired coordination followed by a tobology borrowed from the crystalline structure (Guntherodt, and Beck, 1981)(26).

(b) Sphere packing :

This model is built mainly by assuming the aggregated atoms of a system in its amorphous phase as a spheres having a certain size and the closest distance of approach for two spheres, (or coordinated), is not smaller than their atomic radii.

The densely random packing (DRP) of homogeneous, coherent and essentially irregular assemblages without vacancy, and large range order like those in crystals as suggested by Bernal in 1959(27) may be applied to determine the structure of many amorphous binary alloys. Figure 2 shows the tetragonal close packed units, such that many polygons may be constructed