

EXTENDED X-RAY ABSORPTION FINE STRUCTURE EVIDENCE FOR HOMOPOLAR BONDING IN AMORPHOUS Cd-As AND Zn-P

A. BURIAN

Department of Solid State Physics, Polish Academy of Sciences
Wandy 2, 41-800 Zabrze, Poland

Local atomic arrangement in evaporated amorphous Cd-As and Zn-P films was investigated by extended X-ray absorption fine structure. Results of modelling indicate that bonds between atoms of the same kind occur for both (Cd,Zn)-rich and (As,P)-rich compositional regions. This specific chemical ordering, much alike to that in the corresponding crystalline polymorphs, appears to play a predominant role in determining of the local structures in these materials.

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In the recent years the extended X-ray absorption fine structure (EXAFS) technique has proved to be very powerful tool for local structure analysis of disordered materials like amorphous semiconductors [1-3]. The main advantage of this technique is its ability to probe the environment of a selected atomic species. Therefore, the use of EXAFS is especially of interest in case of multicomponent materials in which different partial radial distribution functions (RDF) are merged in the near-neighbour coordination sphere.

For $A^{III}B^V$ amorphous semiconductors as Ga-P and In-P it was found that A-A, B-B bonds appear to be formed apart from A-B bonds, which should be favoured in these systems [1, 2]. Bonds between alike atoms are called "wrong bonds" and their detailed characterization is necessary to interpret correctly the electronic properties of these materials. The previously performed large-angle X-ray scattering (LAXS) investigations on the Cd-As and Zn-P amorphous films showed that the tetrahedral models, in which the partial Cd(Zn)-Cd(Zn), Cd(Zn)-As(P) and As(P)-As(P) contributions are involved in the first RDF peak, account for the experimental data [4, 5].

In order to study precisely the environment of individual atoms, the EXAFS experiments were carried out at both the As and Zn *K*-edges for the Cd-As films with composition from 45 to 82 at% As and the Zn-P films containing 47 and 68 at% P. The measurements were performed on the DCI synchrotron radiation facility at LURE (Orsay, France). The experiments and the data treatment were described in detail elsewhere [6-8].

The oscillatory part of the absorption coefficient in the single-scattering approximation, assuming Gaussian distribution of interatomic distances, is given by the expression [6]:

$$X(k) = \sum_j S_i N_j F_j(k) \exp(-2k^2 \sigma_j^2) \exp(-2r_j/\lambda_j) \frac{\sin[2kr_j + \Phi_{ij}(k)]}{kr_j^2},$$

in which $k = [8\pi^2 m(E - E_0)/h^2]^{1/2}$, m is the mass of electron, h is Plank's constant, E_0 is the energy threshold, S_i is the amplitude scaling factor included to consider multielectron excitation at absorbing atom i , F_j is the backscattering amplitude from N_j neighbours of the j -th type at distance r_j from absorbing atom, λ_j is the electron free path, σ_j is the standard deviation of the interatomic distance, Φ_{ij} denotes the total phase shift.

Several models were tested to reconstruct the first coordination sphere around As and Zn atoms [7, 8]. The least-squares fitting procedure was applied to analyse the measured spectra. The resulting parameters together with the fitting uncertainties are collected in Table I.

TABLE I

The best fit parameters for the Cd-As amorphous films.

Sample	r [Å] (±0.03)	N (±0.5)	σ [Å] (±0.02)	S (±0.2)	E_0 [eV] (±2)	R
Cd ₅₅ As ₄₅	As-As	2.43	0.90	0.05	2.00	0.0017
	As-Cd	2.69	2.10	0.08		
	As-Cd	2.91	1.00	0.11		
Cd ₅₀ As ₅₀	As-As	2.44	1.00	0.06	1.05	0.0055
	As-Cd	2.68	2.00	0.10		
	As-Cd	2.92	1.00	0.11		
Cd ₃₆ As ₆₄	As-As	2.42	1.75	0.06	2.00	0.0072
	As-Cd	2.66	1.50	0.07		
	As-Cd	2.76	0.75	0.14		
Cd ₂₆ As ₇₄	As-As	2.44	2.50	0.07	1.20	0.0047
	As-Cd	2.67	1.50	0.10		
Cd ₁₈ As ₈₂	As-As	2.44	3.00	0.07	0.70	0.0017
	As-Cd	2.67	1.00	0.07		

In order to fit the experimental data for the Cd-rich compositions it was necessary to introduce two slightly different As-Cd subshells and one As-As shell. For the films containing 74 and 82 at% As the two-shell models with one As-As

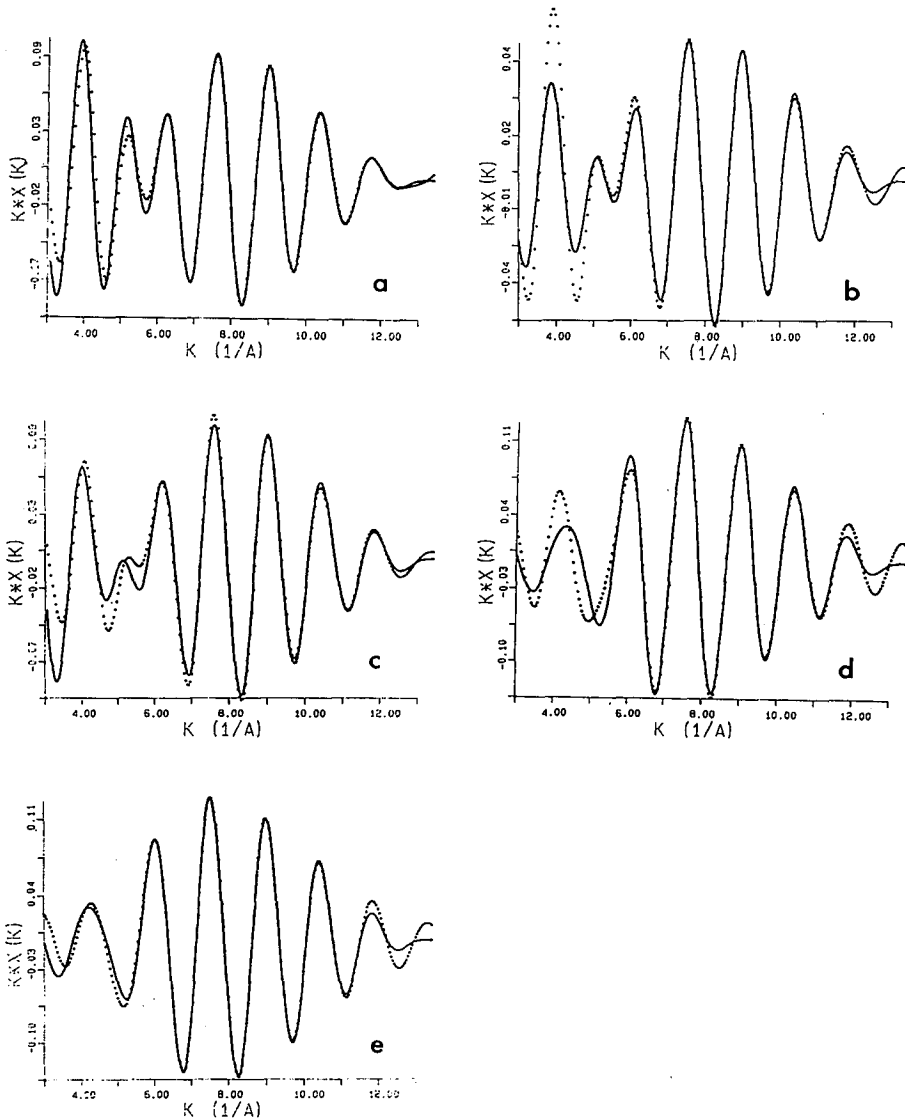


Fig. 1. The $kX(k)$ calculated functions (the three-shell model for (a) $\text{Cd}_{55}\text{As}_{45}$, (b) $\text{Cd}_{50}\text{As}_{50}$, (c) $\text{Cd}_{36}\text{As}_{64}$ and the two-shell model for (d) $\text{Cd}_{26}\text{As}_{74}$, (e) $\text{Cd}_{18}\text{As}_{82}$ — dotted line) superimposed on the experimental data (solid line).

and one As-Cd shell matches satisfactorily the data. The As-As distances are the same within the errors for all compositions. The appreciable contraction of the As-Cd distance is observed for the As-rich films. Such a trend was found from the LAXS studies and was explained by the structural change [4].

For the films containing 45 and 50 at% As the distorted tetrahedral model

based on the CdAs type structure [4] describes satisfactorily As environment. The near-neighbours coordination sphere of the films at 74 and 82 at% As looks much alike to that of crystalline CdAs₂. The compositions close to 64 at% As can be regarded as intermediate between two Cd- and As-rich structural regions. The results of the fits are superimposed on the experimental data in Fig. 1.

Assuming tetrahedral coordination and the bond consistency condition: $c_A N_{A-B} = c_B N_{B-A}$ (c_A and c_B are the atomic concentrations), the presence of the Cd-Cd contribution is expected for the Cd-rich compositions. In order to verify this hypothesis, the environment of Zn atoms was studied. The best fit parameters are shown in Table II. The threshold energy difference ΔE_0 was evaluated

TABLE II
The best fit parameters for the Zn-P amorphous films.

Sample	r [Å] (±0.03)	N (±0.5)	σ [Å] (±0.02)	R	
Zn ₅₃ P ₄₇ Zn-P	2.39	3.12	0.096	0.0126	
Zn ₃₂ P ₆₈ Zn-P	2.39	3.75	0.098	0.0085	
Zn ₅₃ P ₄₇	Zn-P	2.38	3.00	0.093	0.0032
	Zn-Zn	2.79	1.00	0.135	
Zn ₃₂ P ₆₈	Zn-P	2.39	3.75	0.098	0.0067
	Zn-Zn	2.81	0.25	0.099	

$\Delta E_0 = -1.15$ eV for Zn₅₃P₄₇ and -0.125 eV for Zn₃₂P₆₈
(evaluated according to [9]). $S = 0.72$ (theoretical value as given in [10, 11]).

using the method proposed by Lee and Beni [9]. The amplitude scaling factor S was taken from Carlson's tables [10], experimentally verified by Stern, Bunker and Heald [11].

For the Zn₅₃P₄₇ film the fit yielded 1 Zn atom and 3 P at around Zn. As the content of P increased to 68 at%, the number of the Zn-Zn bonds is almost completely reduced within method precision and the fit converges to the N_{Zn-P} coordination number close to four. Adding the Zn-Zn contribution weighted by 0.25 improves slightly the fit when compared with the one-shell Zn-P model [7]. The best fits of the two-shell model are shown in Fig. 2.

Changing of the chemical composition of the Cd-As and Zn-P amorphous films leads to two different types of local ordering. The obtained coordination numbers around both As and Zn indicate that II-II, V-V and II-V bonds are formed for the Cd(Zn)-rich films. Such bonds are characteristic of the II-V compounds with 1:1 stoichiometry and their nature departs somewhat from the usual concept of semiconducting bond [4, 5].

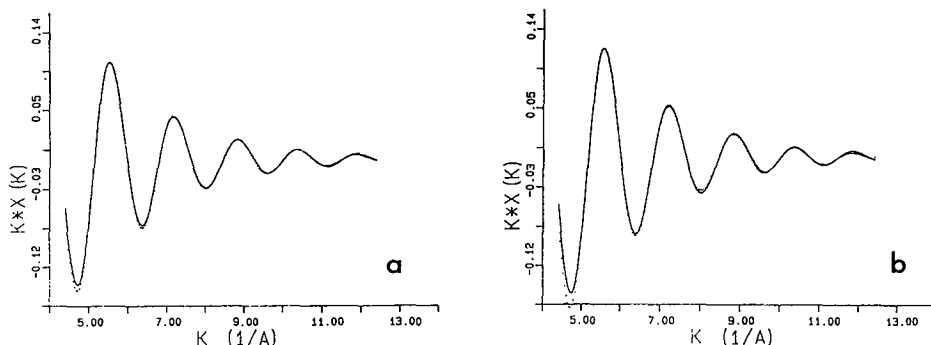


Fig. 2. The two-shell best fit (dotted line) and experimental $kX(k)$ (solid line) functions for (a) $Zn_{53}P_{47}$ and (b) $Zn_{32}P_{68}$.

For the As(P)-rich films the metal-metal contribution is practically excluded. This tendency can be understood considering the bond scheme in the corresponding 1:2 crystalline polymorphs, in which the As(P) atoms are coordinated by two As(P) and two Cd(Zn), whereas Cd(Zn) has 4 As(P) as the nearest neighbours [4, 5].

The bonds between alike atoms are not considered in terms of chemical disorder and the amorphous II-V systems can be regarded as a new family of non-crystalline semiconductors with the specific structure.

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