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ABSTRACT

The local structure of InGaAsP quaternary alloys epitaxially grown on InP substrates has been studied by EXAFS and near-edge structure. The bimodal distribution of bondlength at both cation (In,Ga) and anion (As,P) sites were confirmed. The bondlengths were found to deviate from the VCA average by 2.4-5.5 % whereas they deviate from those in pure binary compounds by only 0.9~1.6 %. These deviations were found to be constant within 0.4 % over a wide range of composition when the VCA average is kept constant. Two cation species (Ga,In) and anion species (As,P) are expected to be randomly distributed on each sublattices. The average interatomic distance calculated from the weighted sum of bondlengths agrees the VCA average over a wide range of alloy composition. These results imply that lattice relaxation of lattice-matched quaternary alloys can be realized by only bond-bending.

INTRODUCTION

InGaAsP alloy semiconductors lattice-matched to InP have been extensively studied and developed for their use in the optical communication system in the 1-μm wavelength region. The alloy composition dependence of the fundamental properties have been experimentally studied and estimated using a linear interpolation from the parameters of the constituent binary compounds or the virtual crystal approximation (VCA). To understand the characteristic properties of these alloys such as a bowing of optical gap, the atomic-scale structure within a few Å around each constituent species of atom is essential. The bimodal distribution of bondlength in pseudobinary semiconductor alloys has been predicted by Fong. et al. [1] and experimentally confirmed by Mikkelsen et al. [2] using EXAFS. Previous EXAFS studies of ternary alloys such as InGaAs revealed that the bondlength is rather close to that in constituent binary compound deviating from the average interatomic distance obtained from X-ray data and the VCA. In this study, the local structure and lattice relaxation in quaternary alloys have been investigated, for which the VCA is expected to be more valid than for the ternary system because of more random distribution of chemical bonds.

EXPERIMENTAL

InGaAsP quaternary alloys and InGaAs ternary alloys lattice-matched to InP were grown by liquid phase epitaxy (LPE) at 625-635°C with a typical thickness of 5000 Å. For the EXAFS measurements the InP substrate was thinned down to 50 µm and attached to a silicon-holder with a hole to pass the transmitted X-rays through it. Ga and As K-edge X-ray absorption spectra were obtained utilizing synchrotron radiation from the 2.5 GeV storage ring at the Photon Factory and a fluorescence EXAFS apparatus [3]. X-rays from the storage ring were monochromatized and focused horizontally at the sample by a sagittally bent crystal monochromator [4]. Fluorescence X-rays were collected by a scintillation detector array which covers 18 % of the total solid angle. The energy resolution was 2 eV at 9 keV and a typical incident photon flux of 10^{10} photons/sec was obtained.

RESULTS AND DISCUSSION

The equi-energy gap contour for InGaAsP quaternary alloys is illustrated in Fig. 1. If the alloy composition is chosen along the dashed lines, the lattice constant can be matched to those of InP or GaAs. In this study, the composition was carefully chosen so that the lattice constant matches that of InP. (a), (b), and (c) denote the compositions for $In_{0.53}Ga_{0.47}As$, $In_{0.60}Ga_{0.40}As_{0.89}P_{0.11}$, and $In_{0.74}Ga_{0.26}As_{0.58}P_{0.42}$, respectively. Figure 2 shows the results of Fourier transform of As K-edge EXAFS oscillations. The first peak located at 2.3 Å consists of two shells. These two distances correspond to As-Ga bond and As-In bond, respectively.

The nearest neighbor contribution is back-Fourier transformed into a k-space and fitted by a single scattering formula [5]. The phase shift functions for Ga-As, Ga-P, As-Ga, and As-In pair were determined by fitting the Ga and As K-edge EXAFS data for GaAs, GaP, and InAs with the same formula using the theoretical backscattering amplitude and known lattice parameters. Utilizing the experimental phase shift functions and theoretical amplitude functions, the bondlengths and Debye-Waller factors were obtained by a least-squares fit.

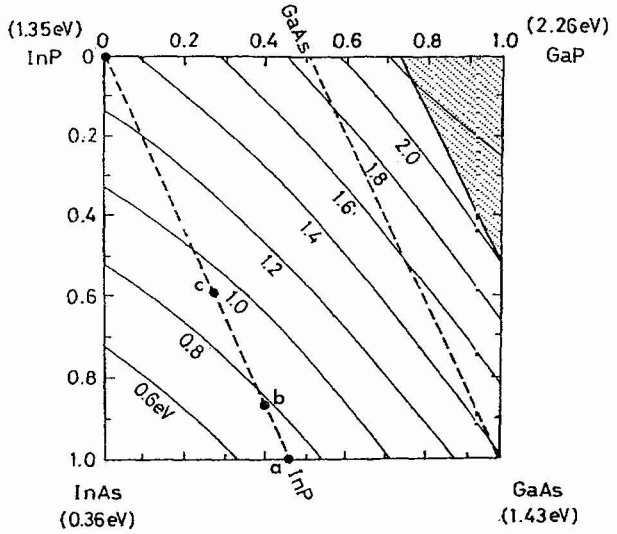

Fig. 1 Equi-energy gap contour of InGaAsP alloys.

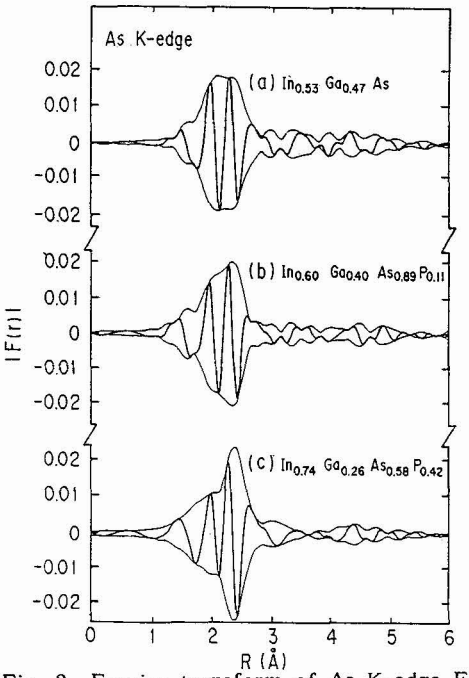

Fig. 2 Fourier transform of As K-edge EXAFS.

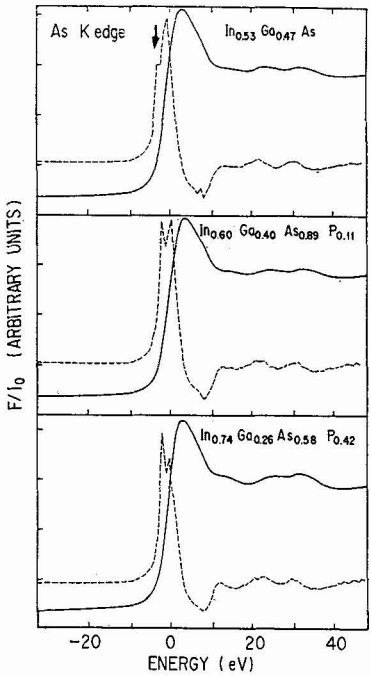

Fig. 3 As K-XANES spectra.

Various ratios of cation species (Ga,In) and anion species (As,P) were tested in the least squares fit fixing the total coordination number of four. The best fit was obtained when the ratio proportional to the alloy composition was used, indicating that each sublattice is randomly distributed by the two species.

In Table I, the results of this least-squares analysis are summarized. The Ga-As bondlength in ternary or quaternary alloys is considerably (ca. 0.08 Å) shorter than the average interatomic distance of 2.54 Å but rather close to that of pure GaAs (2.448 Å) indicating the existence of bond alternation in quaternary alloys. The Ga-As bondlength in InGaAsP alloys lattice-matched to InP is unchanged within 0.001 Å.

The Ga-P bondlength in $In_{0.74}Ga_{0.26}As_{0.58}P_{0.42}$ is shorter than the average interatomic distance by 0.14 Å while it is longer than that of pure GaP by 0.035 Å. The As-In bondlength in InGaAsP alloys is longer than the average interatomic distance by 0.07-0.08 Å but shorter than that of pure InAs by 0.23 Å. The In-P bondlength in InGaAsP alloys is not available but it is estimated to be close to the In-P distance in pure InP, or the average interatomic distance (2.5412 Å) since the quaternary alloys are lattice-matched to InP. Inspecting the values given in Table I, it is clear that the bondlengths are insensitive to the average coordination number of two cation or anion species. The Debye-Waller factor of each bond in InGaAsP alloys was found to be close to that in pure binary compounds.

Figure 3 shows the As K near-edge spectra of InGaAsP alloys. Solid and dotted lines indicate the raw spectra and their first derivatives. Although no appreciable edge shift has been observed between alloys and pure binary compounds, a new doublet structure is observed in the derivative spectra at the absorption threshold, which is not observed in pure InAs or the 1:1 mixture of InAs and GaAs. The peak located at the lower energy increases its strength on going from (a) to (b) indicating that this structure is caused by alloying with indium. The Td symmetry around As atom in InGaAsP alloys is expected to be distorted because of In atom, which might split the degenerated conduction band by a crystal field effect or enhance the s-d transition by mixing with p-states.

Table I. Bondlengths in $In_{1-x}Ga_xAs_{1-y}P_y$

Specimen	Bondlengths (Å)			
	Ga-As	Ga-P	As-Ga	As-In
(a)x=0.47 y=0	2.47	-	2.47	2.60
(b)x=0.40 y=0.11	2.47	-	2.47	2.60
(c)x=0.26 y=0.42	2.47	2.40	2.47	2.59
VCA*	2.54	2.54	2.54	2.54
GaAs*	2.448		2.448	
GaP*		2.360		
InAs*				2.623

*Obtained by x-ray diffraction.

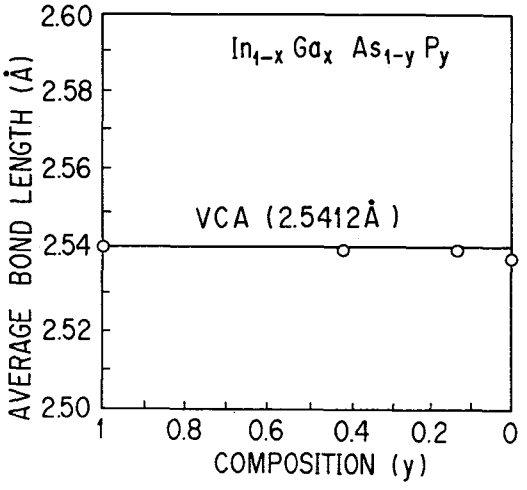

Fig. 4 Average bondlengths in InGaAsP quaternary alloys.

The microscopic average bondlength is defined as the sum of four bondlengths weighted by the number of each bonds. Since the two cation species (Ga,In) and anion species (As,P) are expected to be randomly distributed on each sublattices, bond pairs are assumed to be randomly distributed. No like-atom bonds are considered. The numbers of four bonds, i.e. Ga-As, Ga-P, In-As and In-P, were calculated from the alloy composition. Figure 4 shows the obtained microscopic average which is plotted for the three quaternary alloys. The solid line indicates the average VCA interatomic distance (macroscopic average). The obtained average bondlength agrees the macroscopic average surprisingly well. These results suggest that the quaternary alloys are substitutionally random and relaxed by only the bond-bending when the composition is chosen so that the lattice constant is fixed [6].

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