

Ion beam-induced and thermal reactions at Fe:GaAs interface

P G BILURKAR

Department of Physics, University of Poona, Pune 411 007, India

MS received 14 November 1990

Abstract. Ion beam-induced and thermal reactions at Fe:GaAs interface are studied by using conversion electron Mössbauer spectroscopy and small angle X-ray diffraction measurements. A thin film of Fe (enriched to 30% in ^{57}Fe Mössbauer isotope) was deposited in UHV environment on $\langle 100 \rangle$ oriented semi-insulating GaAs substrates. Some of the samples were ion-mixed by 130 keV Ar^+ ions at dose values of 3×10^{15} and 10^{16} ions/cm². The as-deposited and ion-mixed samples were annealed at different temperatures up to a maximum of 500°C. It was observed that ion mixing led to precipitation of disordered and/or defective binary phase along with ferromagnetic Fe_3GaAs ternary phase which upon vacuum annealing at 500°C for 1 h leads to a mixture of structurally well-defined Fe_3Ga , FeAs and FeAs_2 phases. The combined analysis of Mössbauer and X-ray data is shown to reveal the location of the phases below the sample surface. The mechanism for phase formation and associated reaction kinetics at Fe/GaAs interface is discussed in the light of the experimental results.

1. Introduction

Investigation of metal-compound semiconductor interface is an exciting area of research from the standpoint of both science and technology (Palmsrom and Morgan 1985; Ruckman *et al* 1986; Genut and Eizenberg 1987). From the viewpoint of science the presence of compound as one of the participants in processing leads to interesting questions such as the possibility of ternary phase formation, site selectivity in diffusion processes, role of chemical driving force in phase precipitation etc. Technologically, such studies are of critical importance for obtaining practical devices via realization of good ohmic contacts (Palmsrom and Morgan 1985). In this context it is not only important to know the nature of phase(s) formed by interface reactions but also the stability of such phase(s) under treatments at different temperatures to which the sample may be subjected during sequential treatments (Prinz 1985; Sands *et al* 1987). It is also important to know whether the phase formation process can be controlled and tailored by adopting to newer methods of interface processing such as ion beam mixing.

In the present work we have studied ion beam and thermal reactions at Fe/GaAs interface. This system has been of interest for some time in view of the fact that Fe can be grown epitaxially on GaAs (Prinz and Krebs 1981; Chambers *et al* 1986; Randal *et al* 1987; Krebs *et al* 1987). Also studies have been reported on Mössbauer characterization of Fe-doped GaAs and these have revealed that depending on the processing conditions this system exhibits several interesting magnetic properties (Isaev–Ivanov *et al* 1975; Seregin *et al* 1979). Moreover there is a fair data-base available on Fe-Ga, Fe-As binary systems to enable reasonable analysis of results (Katsuraki and Achiwa 1966; Newkirk and Tsuei 1971; Kawamiya *et al* 1972; Kulshreshtha and Raj 1979; Yuzuri *et al* 1980; Kawamiya and Adachi 1986). Further, Fe belongs to the 3d transition metal family of elements such as Co and

Ni, which are of significant interest in the context of semiconductor contacts and it has a suitable Mössbauer isotope (^{57}Fe) which can reveal several unique microscopic features via knowledge of hyperfine interaction parameters (Ogale *et al* 1985, 1987). In the present work the surface layer-sensitive technique of conversion electron Mössbauer spectroscopy (CEMS) (Ogale *et al* 1985) has been used in conjunction with the small angle X-ray diffraction technique employing Seeman Bohlin geometry to bring out the nature of thermal and ion-beam induced (130 keV, Ar^+ ions) reactions at Fe/GaAs interface.

2. Experimental

Liquid encapsulated Czochralski (LEC) grown semi-insulating GaAs substrates in $\langle 100 \rangle$ orientation were used in the present work. The substrates were degreased in organic solvent, etched in a mixture of $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:1:40 by vol.) and rinsed in a mixture of $\text{NH}_4\text{OH}:\text{H}_2\text{O}$ (1:10 by vol.) before putting into UHV system for iron deposition. A 700 Å thick layer of iron enriched to 30% in ^{57}Fe concentration was deposited using conventional thermal evaporation technique. The background pressure during deposition was below 10^{-7} torr. The thickness was measured using Inficon XTC crystal monitor. The samples were then ion-beam-mixed with 130 keV Ar^+ ions at two different dose values viz 3×10^{15} ions/cm² and 1×10^{16} ions/cm². Ion current during implantation was maintained below $1 \mu\text{A}/\text{cm}^2$ to avoid appreciable heating of the samples. The as-deposited and ion-beam mixed samples were simultaneously annealed in a turbomolecular pumped vacuum system at a pressure $< 10^{-6}$ torr up to a maximum temperature of 500°C. The as-deposited, ion-beam-mixed and subsequently vacuum-annealed samples were studied using CEMS and low angle X-ray diffraction technique. The X-ray data were obtained on a Rigaku Japan unit, (model No. Rotaflex Ru 200B) at a glancing angle of 0.5°. CEM spectra were recorded using a constant acceleration Mössbauer set-up with $^{57}\text{Co}:\text{Rh}$ as the source. The 7.3 keV K-shell conversion electrons emitted within 0.20 μm below the top surface were detected in a continuous gas (helium + 4% ethanol) flow proportional counter. The standard MOSFIT program was used to obtain the best fit values of the hyperfine interaction parameters (MOSFIT).

3. Results and discussion

The low-angle X-ray diffraction pattern of the as-deposited sample taken at glancing angle $\alpha = 0.5^\circ$ is shown in figure 1a. Two such as-deposited samples were ion-beam-mixed (IBM) with 130 keV Ar^+ ions at dose values of 3×10^{15} ions/cm² (IBM1) and 1×10^{16} ions/cm² (IBM2) and the respective spectra are presented in figures 1b, c. CEM spectra for these samples are shown in figure 2. The low-angle X-ray diffraction pattern of the as-deposited sample (figure 1a) shows diffraction lines corresponding to the deposited α -Fe overlayer and GaAs substrate and no sign of any significant interface reaction during deposition. The CEM spectrum of the as-deposited sample (figure 2a) however could be fitted with two doublets which should represent the products of deposition-induced reaction and a sextet having an internal magnetic field value of 330 kOe corresponding to the deposited layer of α -Fe. The hyperfine interaction parameters viz isomer shift (IS) and quadrupole

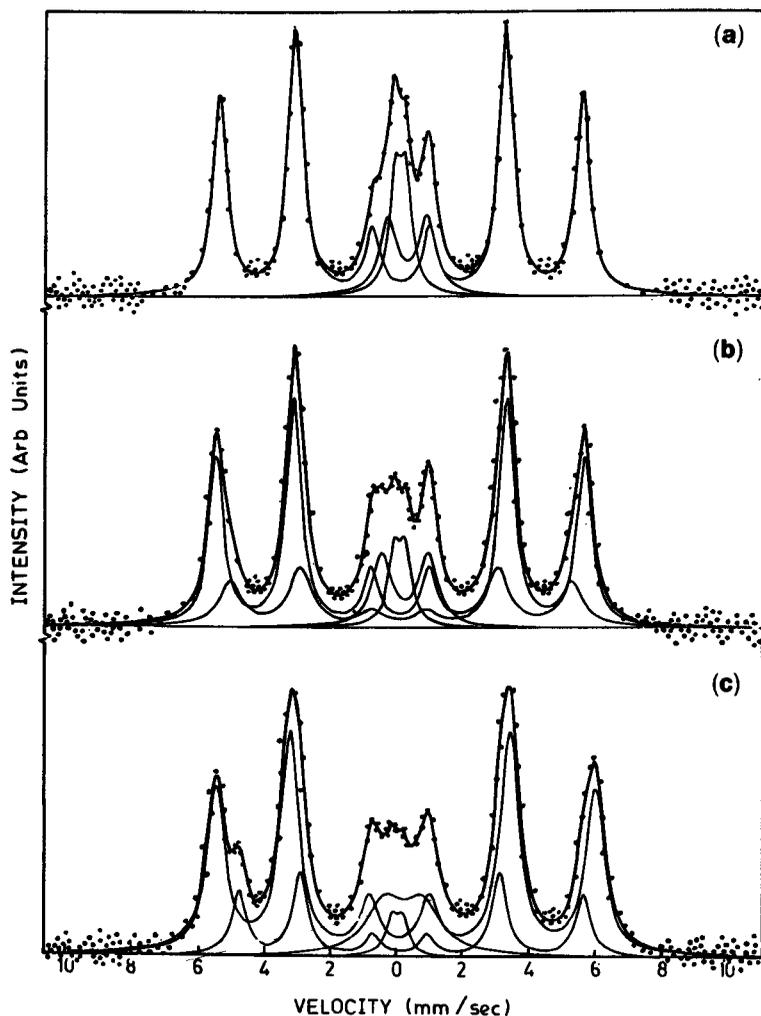


Figure 2. Room temperature CEM spectra of a. as-deposited sample, and ion beam mixed at dose value of b. 3×10^{15} ions/cm² and c. 1×10^{16} ions/cm².

Unfortunately, the Mössbauer parameters of such a phase have not yet been established. Interestingly the CEM spectrum of IBM1 sample shows emergence of an additional sextet having internal magnetic field (IMF) value of 308 kOe. In the light of the X-ray results this low field magnetic component can be possibly attributed to the ternary Fe₃GaAs phase. The Mössbauer results also exhibit broadening of resonance lines due to stoichiometric disorder and the intensity of sextet corresponding to α -Fe is found to be reduced due to ion mixing. It is interesting to observe that the CEM spectrum and X-ray diffraction pattern of IBM2 sample (figures 2c and 1c respectively) do not show any basic changes in their structure except for broadening of resonance lines and diffraction lines, and reduction in diffracted intensity due to enhancement of disorder.

The above analysis defines the initial states of three samples viz as-deposited, IBM1 and IBM2, prior to their being subjected to vacuum-annealing treatment at

various temperatures to investigate the interface reactions. The reaction kinetics of metal-GaAs interface has been considered to be an important aspect in the context of III-V device fabrications. The metallic contacts to these devices have to be in thermodynamic equilibrium with substrate and this can be ensured provided the interface reaction is complete during processing subsequent to the metal deposition. Also rapid interdiffusion of metallic species in GaAs may result in the increase in specific contact resistance if the contact is annealed at higher temperature than the optimum temperature (Kuan *et al* 1983). Thus it becomes necessary to extract the information regarding growth of phases at Fe/GaAs interface and the diffusional behaviour of iron during the annealing process.

The CEM spectrum of the as-deposited sample annealed at 350°C is shown in figure 3a. The overall nature of the spectrum is similar to that of the as-deposited sample (figure 1a); however, it could be fitted with an additional six-line pattern

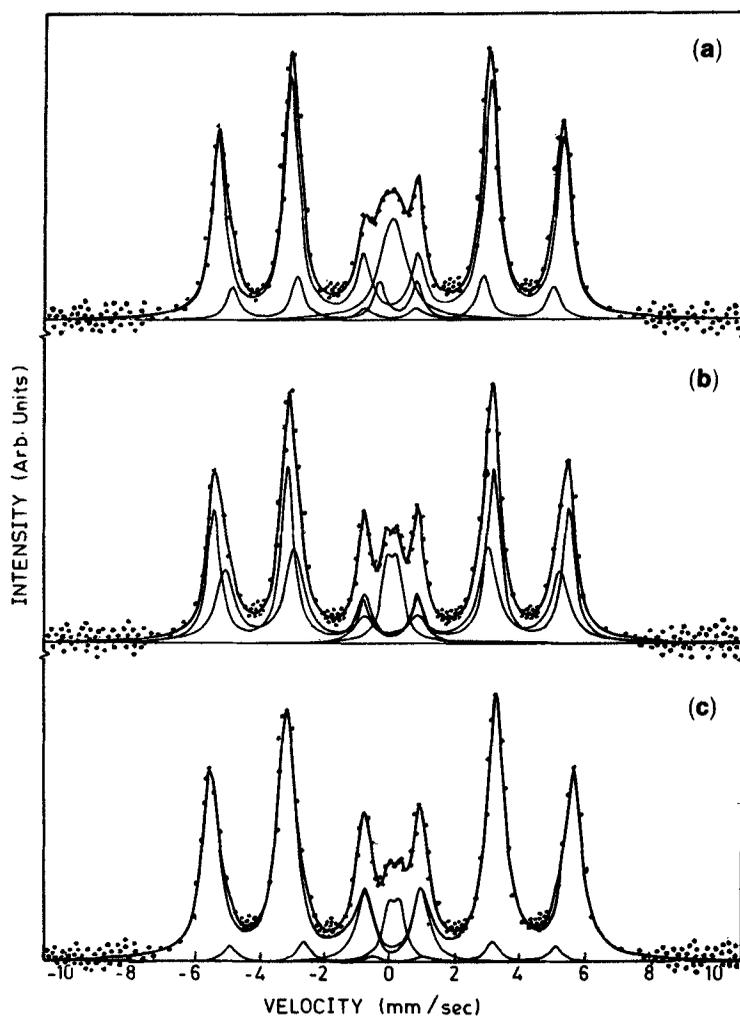


Figure 3. Room temperature CEM spectra of samples annealed at 350°C a. as-deposited sample, and ion beam mixed at dose value of b. 3×10^{15} ions/cm² and c. 3×10^{16} ions/cm².

(IMF = 306 kOe) which can be attributed to the ferromagnetic Fe_3GaAs ternary phase mentioned earlier. The corresponding low-angle X-ray diffraction pattern (not shown) also indicates the formation of the ternary phase. This shows that diffusion of a small amount of iron in GaAs occurs during annealing at 350°C . The CEM spectrum of IBM1 sample annealed at 350°C (figure 3b) does not show any significant changes when it is compared with its initial state (figure 1b). However the IBM2 sample annealed at 350°C exhibits complete diffusion of iron in GaAs leading to the formation of Fe-Ga like magnetic phase (Newkirk and Tsuei 1971) (sextet with magnetic field 346 kOe) and reduction in the intensity of sextet corresponding to the ferromagnetic ternary phase Fe_3GaAs (figure 3c). Thus the diffusion behaviour of iron and the associated thermal reaction kinetics are remarkably different in the case of Fe/GaAs interface which is bombarded by Ar^+

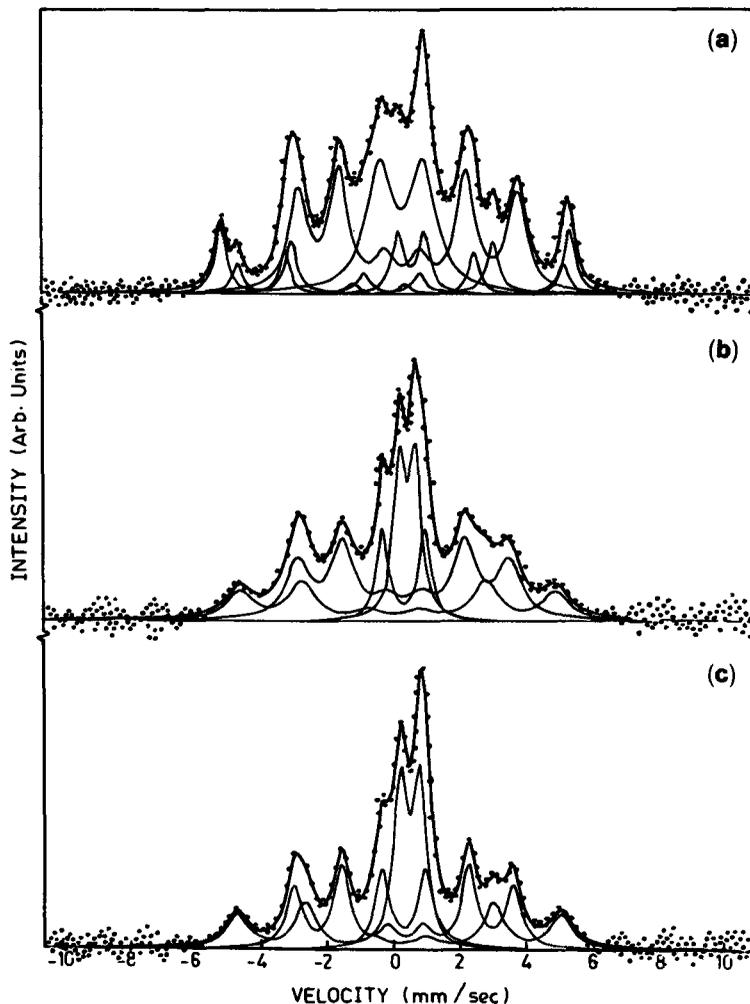


Figure 4. Room temperature CEM spectra of sample annealed at 500°C a. as-deposited sample, and ion beam mixed at dose value of b. 3×10^{15} ions/cm² and c. 1×10^{16} ions/cm².

ions at a dose of 1×10^{16} ions/cm². The reaction model suggested by Palmstrom *et al* (1987) does indicate the formation of ternary phase at low-temperature annealing due to the diffusion of metallic species in GaAs matrix. According to this model the outdiffusion of GaAs as a molecule is unlikely, and therefore the metal species diffuse in GaAs matrix to form ternary phases whereas the dissociation of GaAs molecule at the surface leads to the out-diffusion of Ga and As to form binary phases with metal present in the deposited layer. At high temperatures, Ga and As in ternary phase become significantly mobile and the ternary phase decomposes into binaries. Such a ternary phase formation has also been observed in the case of Co/GaAs, Pd/GaAs, Ni/GaAs interfaces due to low-temperature thermal reaction (up to 370°C) (Sands *et al* 1987; Palmstrom *et al* 1987).

In order to obtain further information about the reaction kinetics at Fe/GaAs interface, the as-deposited, IBM1 and IBM2 samples were vacuum-annealed at 500°C for 1 h and the corresponding CEM spectra are presented in figures 4a–c respectively. The Mössbauer spectrum shown in figure 4a could be fitted with three sextets and two doublets whereas the remaining two spectra (figures 4b,c) could be fitted with only two sextets and two doublets. The hyperfine interaction values of all these fitted components are presented in table 1. The sextet having an IMF value of 328 kOe in the case of the as-deposited and annealed sample corresponds to α -Fe and the absence of this sextet in annealed IBM1 and IBM2 samples indicates complete diffusion of α -Fe in GaAs matrix. The presence of other two magnetic components in all Mössbauer spectra (figure 4) corresponds to formation of BCC Fe₃Ga phase which contains two non-equivalent sites for iron (A-site and D-site) (Kawamiya *et al* 1972). The formation of Fe₃Ga phase is also confirmed from the low-angle X-ray diffraction results obtained for all these three samples annealed at 500°C (figure 5). It is interesting to point out that the X-ray results on ion-mixed samples (figures 5b,c) show presence of ternary Fe₃GaAs phase. Such a phase is not seen in the corresponding Mössbauer data (figures 4b,c). This means that in the ion-mixed sample the ternary phase is formed at a depth greater than that accessible by the CEMS technique viz 0.20 μ m. In the case of the as-deposited and annealed sample, however, the ternary phase could not be observed either by Mössbauer (figure 4a) or by X-ray diffraction technique (figure 5a).

All these results together suggest that in the case of the as-deposited and annealed sample, the diffusion-limited reactions are responsible for the formation of Fe₃GaAs phase and subsequent high-temperature annealing dissociates the ternary phase into binary phases. For the ion-mixed samples, the ternary phase persists in

Table 1. Hyperfine interaction values.

Samples annealed at 500°C	*IS (mm/s)	QS (mm/s)	*IS (mm/s)	QS (mm/s)	IMF (kOe)
As-deposited	0.49	0.76	0.20	1.32	308, 205
3×10^{15} ions/cm ² (IBM1)	0.53	0.53	0.25	0.80	300, 203
1×10^{16} ions/cm ² (IBM2)	0.42	0.59	0.17	1.16	305, 205
Values quoted in literature	0.43	0.55	0.25	0.89	312, 205
Reference	(FeAs) <i>a</i>		(FeAs ₂) <i>b</i>		(Fe ₃ Ga) <i>c</i>

*Isomer shifts are w.r.t α -Fe; ^a Kulshreshtha and Raj 1979; ^b Yuzuri *et al* 1980; ^c Kawamiya *et al* 1972.

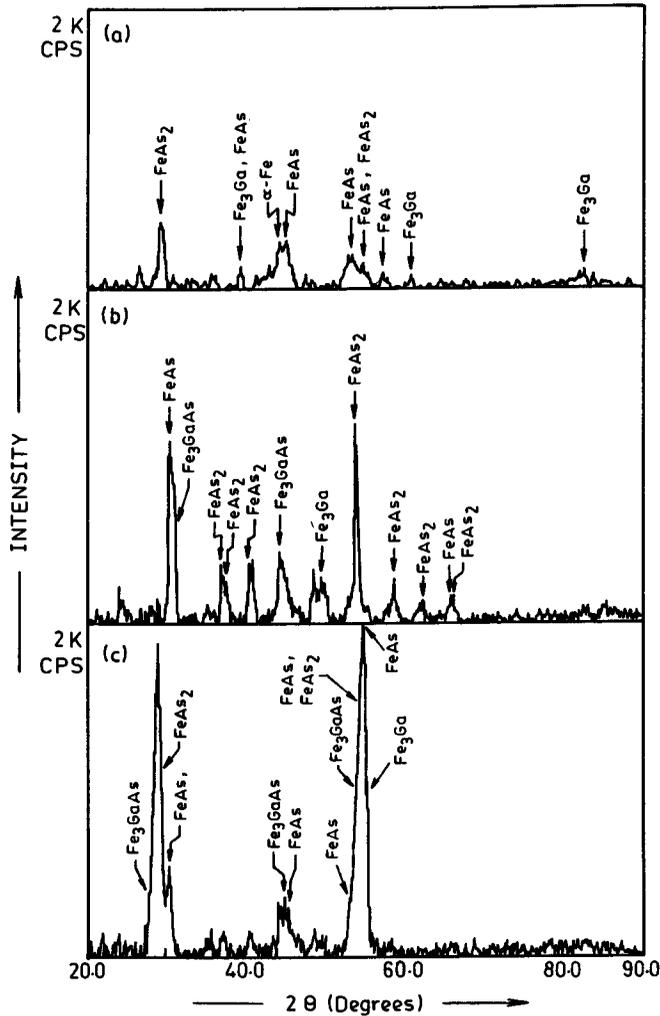


Figure 5. Small angle X-ray diffraction patterns of samples annealed at 500°C a. as-deposited sample, and ion beam mixed at dose value of b. 3×10^{15} ions/cm² and c. 1×10^{16} ions/cm².

the deeper region of the sample even after high temperature anneals, possibly as a consequence of an interplay of the rate of decomposition of the phase and its formation due to constant seeding of iron atoms via diffusion. It is important to point out that the hyperfine interaction parameters of the phases formed in the ion-mixed samples upon annealing at 500°C correspond to those of stoichiometric and structurally well-defined phases. For instance, the doublet with IS of 0.25 mm/s and QS of 0.80 mm/s in the CEM spectrum of annealed IBM1 sample (figure 4b) corresponds to stoichiometric FeAs₂ binary phase (Yuzuri *et al* 1980), whereas the doublet with IS of 0.42 mm/s and QS of 0.59 mm/s in the IBM2-annealed sample (figure 4c) shows the precipitation of stoichiometric FeAs phase (Kulshreshtha and Raj 1979).

Finally, it is necessary to comment on our results in the context of the reaction

model suggested by Palmstrom *et al* (1987) for metal/GaAs interfacial reactions. The diffusion of iron into GaAs matrix causing formation of Fe₃GaAs, and out-diffusion of Ga and As resulting in formation of FeAs, FeAs₂ and Fe₃Ga binary phases are found to be the two competing processes during thermal reactions. In the as-deposited and subsequently-annealed samples, the Fe-indiffusion dominates at low-temperature anneals (350°C) forming Fe₃GaAs ternary phase. However, at high temperature anneals (500°C) the dissociation of ternary phase and the out-diffusion of Ga and As becomes predominant leading to the precipitation of only binaries. Though the results of ion-beam mixed and subsequently annealed samples are consistent with the reaction model, the diffusion behaviour of iron in GaAs matrix is observed to be significantly modified. The iron in-diffusion is always found to be a dominant mechanism of interfacial reactions leading to the formation of ternary phase. For high-temperature anneals, however, the precipitation of ternary phase is found to be only in deeper regions (>0.20 μm) of GaAs samples, whereas in the near interface regions the growth of the binaries is observed.

4. Conclusions

Conversion electron Mössbauer spectroscopy and small-angle X-ray diffraction techniques were used to investigate ion beam-induced and thermal reactions at Fe/GaAs interface. The as-deposited sample and ion-mixed samples exhibited different diffusional behaviour of iron in GaAs matrix leading to the growth of binary and/or ternary phases. The annealing of ion-mixed samples at 500°C resulted in the growth of stoichiometric and structurally well-defined FeAs, FeAs₂ and Fe₃Ga phases.

Acknowledgements

The author is grateful to Prof. Chris Palmstrom for suggesting this problem. The author also appreciates all the help and guidance provided by Prof. S B Ogale and Dr S M Kanetkar during this research. The author is also thankful to the Department of Science and Technology for financial support.

References

- Chambers S A, Xu F, Chen H W, Vitomirov I M, Anderson S B and Weaver J H 1986 *Phys. Rev.* **B34** 6605
- Genut M and Eizenberg M 1987 *Appl. Phys. Lett.* **50** 1358
- Godbole V P, Chaudhari S M, Ghaisas S V, Kanetkar S M, Ogale S B and Bhide V G 1985 *Phys. Rev.* **B31** 5703
- Harris I R, Smith N A, Cockayne B and MacEvan W R 1987 *J. Cryst. Growth* **82** 450
- Isaev-Ivanov V V, Masterov V F, Nasledov D N and Yarmarkin V K 1975 *Sov. Phys. Solid State* **16** 1342
- Katsuraki H and Achiwa N 1966 *J. Phys. Soc. Jpn* **21** 2238
- Kawamiya N and Adachi K 1986 *J. Appl. Phys.* **55** 634
- Kawamiya N, Adachi K and Nakamura Y 1972 *J. Phys. Soc. Jpn* **33** 1318
- Krebs J J, Jonker B T and Prinz G A 1987 *J. Appl. Phys.* **61** 2596
- Kuan T S, Batson P E, Jackson T N, Rupprecht H and Wilkie E I. 1983 *J. Appl. Phys.* **54** 6952
- Kulshreshtha S K and Raj P 1979 *J. Phys. F: Metal Phys.* **9** 2253

- MOSFIT Program originally written by E Kreber and adopted for an ICL 1904S computer by S K Date, NCL, Pune
- Newkirk L R and Tsuei C C 1971 *J. Appl. Phys.* **42** 5250
- Ogale S B, Ghaisas S V, Kanetkar S M and Bhide V G 1985 *Proc. Indian Nat. Sci. Acad.* **A51** 211 .
- Ogale S B, Joshee R, Godbole V P, Kanetkar S M and Bhide V G 1985 *J. Appl. Phys.* **57** 2915
- Ogale S B, Phase D M, Patil P P, Chaudhari S M, Kanetkar S M, Ghaisas S V, Bhide V G and Date S K 1987 *Phys. Rev.* **B35** 1593
- Palmstrom C J and Morgan D V 1985 in *Metallizations for GaAs devices and circuits* (eds) M J Howes and D V Morgan (New York: Wiley) chap. 6
- Palmstrom C J, Chang C C, Yu A, Galvin G J and Mayer J W 1987 *J. Appl. Phys.* **62** 3755
- Prinz G A 1985 *Phys. Rev. Lett.* **54** 1051
- Prinz G A and Krebs J J 1981 *Appl. Phys. Lett.* **39** 397
- Randal W *et al* 1987 *Appl. Phys. Lett.* **51** 285
- Ruckman M W, Joyce J J and Weaver J H 1986 *Phys. Rev.* **B33** 7029
- Sands T, Keramidas V G, Yu K M, Washburn J and Krishnan K 1987 *J. Appl. Phys.* **62** 2070
- Seregin P P, Nasredinov F S and Bakhtiyarov A SH 1979 *Phys. Status Solidi* **B91** 35
- Yuzuri M, Tahara R and Nakamura Y 1980 *J. Phys. Soc. Jpn* **48** 1937