

Argon ion-irradiation effects at the interface of Cu/Fe bilayers

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 4713

(<http://iopscience.iop.org/0953-8984/12/22/304>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 05:10

Please note that [terms and conditions apply](#).

Argon ion-irradiation effects at the interface of Cu/Fe bilayers

J Desimoni[†], G Echeverría[†], G Punte[†], R C Mercader[†], M Behar[‡],
J W Freeland[§]|| and J C Walker[§]

[†] Departamento de Física, Universidad Nacional de La Plata, C C 67, 1900 La Plata, Argentina

[‡] Instituto de Física, Universidade Federal de Rio Grande do Sul, Porto Alegre, Brazil

[§] Department of Physics and Astronomy, The Johns Hopkins University, Homewood Campus, Baltimore, MD 21218, USA

Received 1 November 1999, in final form 5 April 2000

Abstract. Cu/Fe layers produced by molecular beam epitaxy were subjected to 360 keV Ar⁺ irradiation at 180 K and 295 K over a range of ion fluences from 2.0×10^{15} to 5.0×10^{16} ions cm⁻². Rutherford backscattering spectrometry and x-ray diffraction were used to monitor the evolution of the interfaces after each step of irradiation. Up to fluences of approximately 5×10^{15} Ar⁺ cm⁻², at both substrate temperatures, a moderate decrease of the initial Cu edge variance was observed. At higher fluences an inter-diffusion of the layers was noticed. The results are interpreted as being caused by stress effects and plastic deformation.

1. Introduction

Ion-beam bombardment has been used many times to produce solid solutions of immiscible systems. Because of the intricate nature of the processes involved, the ion-beam mixing of layered systems is not completely understood yet. Several models that take into account thermodynamic parameters [1–4], like heat of mixing and cohesion energy, explain successfully most experimental results for systems with negative heats of mixing, but fail to interpret those of systems with positive heats. For Cu/Fe, with a positive heat of mixing of $\Delta H_m \approx +15$ kJ mol⁻¹ [5], there is no general agreement about the mechanisms involved in ion-beam mixing experiments [6]. The mixing rates at low temperature cannot be described by ballistic models [7] or by thermal spike models [8] with acceptable accuracy. Other authors [9] suggest that the defects created by irradiation act as sinks that induce mixing, despite the fact that formation of Fe and Cu islands due to segregation was detected by Mössbauer spectroscopy in the same work [9]. Amorphous solid solutions have been observed when multi-layer samples were irradiated [10–12].

To help in the understanding of ion-beam mixing processes in immiscible systems, we have performed irradiation experiments with an Ar⁺ beam of 360 keV on a Cu/Fe bilayer with finer detail at low fluences than similar irradiations reported in the literature [6, 9]. The evolution of the samples was followed by Rutherford backscattering spectrometry (RBS) and x-ray diffraction (XRD).

|| Current address: Advanced Photon Source, Experimental Facilities Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA.

2. Experimental procedure

Samples of Cu/Fe/Cu were grown at room temperature by alternate deposition of Cu and Fe of three layers of 1000 Å thickness, on an Si(111) substrate, using a Perkin–Elmer molecular beam epitaxy apparatus at a pressure lower than 1.0×10^{-10} mbar during deposition. To avoid the formation of Fe–Si metastable phases, the first evaporated layer in contact with the substrate was made of copper.

The layers were bombarded with a 360 keV Ar⁺ ion beam, $R_p = 1400$ Å, $\Delta R_p = 300$ Å, $F_d = 115$ eV Å⁻¹ [13]. This ensures that the Ar projectiles stopped within the Fe layer. Two series of irradiations were performed, keeping the sample holder at temperatures of 180 and 295 K, with fluences (φ) running from $\varphi = 2.0 \times 10^{15}$ to 5.0×10^{16} ions cm⁻² at a current of $1 \mu\text{A cm}^{-2}$.

The dependence on irradiation fluence of the Cu edge variance at the Cu/Fe interface was followed by RBS of 760 keV-alpha particles at 165°. To double-check the RBS results obtained at the lower a-beam energy, the RBS analyses of some selected samples bombarded at low fluences were also repeated at 1.4 MeV at the Centre de Spectrometrie Nucléaire et Spectrometrie de Masse, Orsay, France. Mixing variances ($\Delta\sigma_{mixed}^2 = \sigma^2(\varphi) - \sigma^2(0)$) were quantified subtracting the standard deviation of the as-prepared interface profile sample ($\sigma^2(0)$) from the corresponding one after an irradiation fluence $\varphi(\sigma^2(\varphi))$. This quantity proved to be proportional to $4Dt$.

Samples were also characterized by x-ray diffraction with a Philips 1710 x-ray powder diffractometer using graphite monochromatized CuK α radiation. Data were recorded in the range $30^\circ \leq 2\theta \leq 115^\circ$ in steps of 0.02° with a counting time of 11 s per step. Each set of data was analysed by the Rietveld method [14]. The unit cell constants of the Cu and Fe phases were refined along with sample displacement, the profile coefficients of a pseudo-Voigt function modelling peak shapes, and the overall B factors [14]. Preferred orientation correction was applied using the March–Dollase model [15].

3. Results

Figure 1 shows typical RBS spectra of the as-prepared samples and of those irradiated at 180 K with $\varphi = 6 \times 10^{15}$ and 5×10^{16} Ar⁺ cm⁻². It illustrates the evolution of the interface when subjected to ion-beam irradiation. The contamination observable at the surface of the as-prepared sample was sputtered away during the first step of irradiation ($\varphi = 2 \times 10^{15}$ ions cm⁻²) thus bringing about a sharp top edge of the Cu layer. In addition, the interfacial edge of the Cu and Fe distribution sharpens for $\varphi = 6 \times 10^{15}$ ions cm⁻², but broadens for $\varphi = 5 \times 10^{16}$ ions cm⁻². The sharpening is more important when the substrate is at a temperature of 180 K; the broadening is more noticeable at 295 K. The room temperature experiments were repeated twice on a different set of samples and the same results were obtained.

The mixing kinetics, $4Dt$ versus φ , obtained assuming an error function type profile for the Cu concentration versus depth, are displayed in figure 2 for both substrate temperatures, 180 and 295 K. A non-linear dependence can be observed for the whole range of fluences instead of the linear dependence generally reported for miscible systems and the expected predictions of theoretical models. Two regions can be noted in figure 2: (i) the mixing variance decreases with fluence (i.e., de-mixing is observed) for $\varphi < \varphi_c \approx 5 \times 10^{15}$ Ar⁺ cm⁻², and (ii) the mixing variance increases with fluence for $\varphi > \varphi_c$ at a nearly linear rate.

The x-ray diffraction pattern before irradiation is shown in figure 3. The Rietveld line-profile analysis of the data was performed with a model assuming (111) and (110) preferential

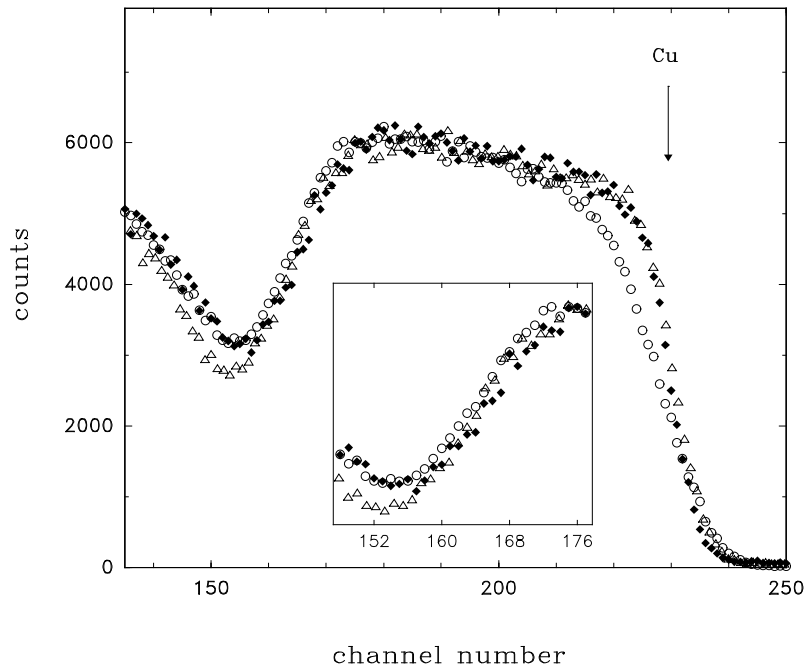


Figure 1. RBS spectra belonging to: as-prepared samples (open circles), and irradiated samples with 360 keV argon ions at 180 K at fluences of $\varphi = 6 \times 10^{15}$ (open up-triangles) and $\varphi = 5 \times 10^{16}$ ions cm^{-2} (solid diamonds). The arrow indicates the position of the Cu front edge. In the inset, the horizontal scale has been expanded to display more clearly the data at the Fe/Cu interface.

orientations of the Cu face centred cubic (fcc) film and of the Fe body centred cubic (bcc) film, respectively. The refinement shows that, except for a broad signal in the $85^\circ < 2\theta < 105^\circ$ region assigned to ε -(Cu,Si) [16], the data can be accounted for by highly oriented Cu ($a_{Cu} = 0.3602 \pm 0.0002$ nm) and Fe ($a_{Fe} = 0.2855 \pm 0.0002$ nm) films. Because of the pronounced preferred orientation, the intensities of the peaks in the high-angle region of the pattern are not simulated by the refinement so accurately as in the low-angle one [14]. This is particularly observable over the range of angles $85^\circ < 2\theta < 105^\circ$ belonging to the broad signal. The evolution of the Cu(111) and Fe (110) peaks with irradiation fluence is shown in figure 4. The copper (a_{Cu}) lattice parameter remains essentially unchanged within experimental errors. The resulting change of the iron (a_{Fe}) lattice parameter with fluence, obtained from the corresponding Rietveld refinements, is plotted in figure 5. A thermal treatment performed at 573 K on the irradiated samples reversed the effect of irradiation on the Fe lattice parameter. No amorphous phases were observed at any fluence.

4. Discussion

The present results show in detail a range of fluences that had been overlooked in previous experiments on the same system [6]. Unlike the behaviour found in most immiscible systems, where either no mixing at all [17–19] or mixing due to collisional processes [6, 9, 20–23] are observed, our results (figure 2) show the two processes already mentioned. We observe that both de-mixing and mixing are temperature dependent. The de-mixing is more pronounced at 180 K while the mixing increases with increasing temperature. This last trend was reported

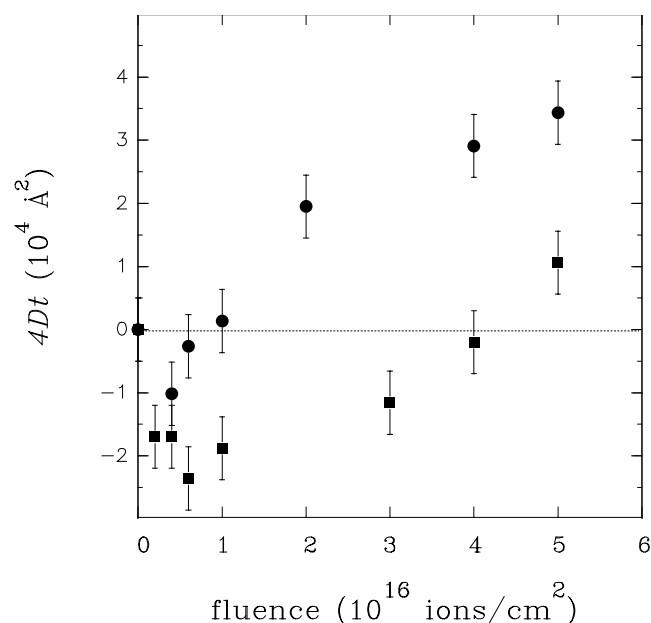


Figure 2. Dependence of the mixing variance on fluence for substrate temperatures of 295 K (solid circles) and 180 K (solid squares).

for Fe/Cu bilayers irradiated at 77 K, 295 K and 550 K [6], contrary to the results of [24] and [18], where a decrease of the amount of mixing with temperature was observed and ascribed to the presence of chemical driving forces.

To our knowledge, the first determination of the mixing kinetics of the Cu/Fe system was performed by Rauschenbach *et al* [6], who used 330 keV Ar and Xe beams to irradiate Cu/Fe bilayers at 80, 300 and 550 K with fluences ranging from 5×10^{15} to 5×10^{16} ions cm $^{-2}$. At these fluences, the de-mixing stage that we observe was not noticed.

Further evidence of de-mixing processes can be inferred from the RBS Ni profile at the lower irradiation fluence of figures 4 and 5 of [17]. These are room-temperature irradiation experiments performed with 200 keV Kr ions on both Pb/Ni and Ni/Pb bilayers [17] ($\Delta H_m = +13$ kJ mol $^{-1}$ [5]). Topological rearrangements at very short distance in ion-beam mixing cascades during phase relaxation, causing a decrease in the initial interface roughness even at low temperatures, could probably be responsible for the de-mixing process as well as a decrease of the roughness of the surface (in contrast to the case of the Ag/Fe system [23]).

In spite of the large number of data reported for Fe/Cu and other immiscible systems [23, 24], there are no determinations of the mixing kinetics, of the mixing efficiency dependence on temperature, or on the deposited energy in the form of nuclear collisions. Therefore, it proves difficult to assess what the relevant processes are, and also to perform quantitative analysis of the mixing rates.

In a former study on Fe/Cu [9], radiation enhanced diffusion was used to interpret results of conversion electron Mössbauer spectroscopy studies of an Fe/Cu interface irradiated with a Kr beam of energies ranging from 30 to 120 keV at only one fluence of 1×10^{16} ions cm $^{-2}$. In this study, the results revealed the formation of Fe precipitates in the Cu layer and vice versa, but no de-mixing was produced by the irradiation. Using the experimentally found extent of mixing and the calculated deposited energy distributions, the authors claim that when most

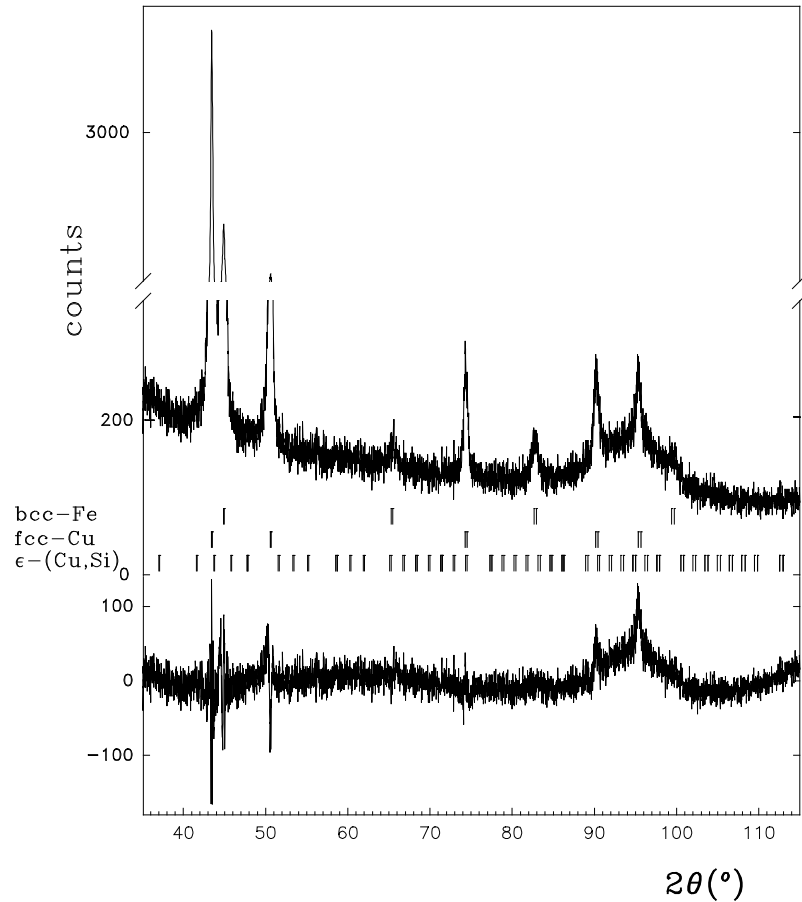


Figure 3. Rietveld profile analysis of the powder diffraction pattern of as-prepared samples. The vertical bars show the line positions of bcc-Fe, fcc-Cu and ϵ -(Cu,Si). The differences between the observed and calculated data are plotted at the bottom.

of the energy deposition takes place in the Fe layer, this region acts as an effective source of vacancies for Cu atoms which migrate into Fe. Besides, increasing the energy deposition in Cu seems to provide internal vacancy formation (and also annealing mechanisms leading to less incorporative diffusion of Fe) and to radiation enhanced diffusion that plays a significant role in the process of ion mixing.

Rauschenbach *et al* [6] reported an increase of mixing with fluence and with increasing temperatures over the whole range of fluences. To explain this behaviour, the authors compared their results with theoretical predictions of the ballistic [7] and thermal spike models [8]. None of these calculations reproduced their data.

In our experiments, for Ar fluences higher than φ_c (figure 2), a linear relationship between $4Dt$ and φ might be established as the simplest dependence. The mixing efficiency ($4Dt/\varphi$) dependence on temperature of our results and those of [6], shown in figure 6, indicates that radiation-enhanced diffusion seems not to be the process responsible for mixing at $T \approx 180$ K, unlike the hypothesis of reference [9].

Calculations of the mixing rate performed with the ballistic model [7] predict

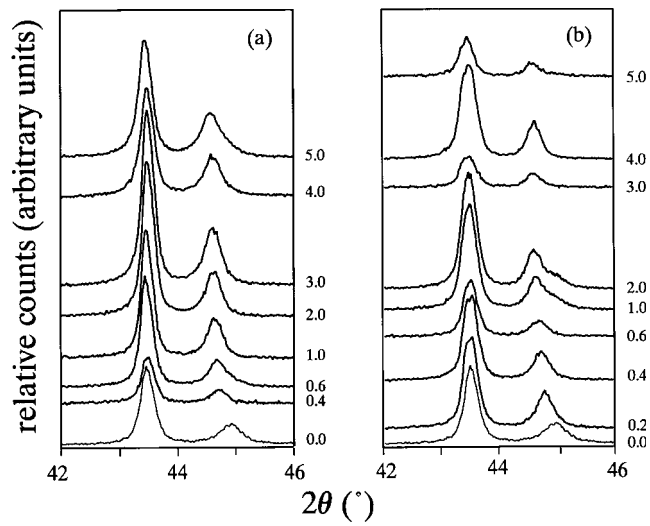


Figure 4. Evolution of the fcc Cu (111) and bcc Fe (110) x-ray diffraction peaks with the irradiation fluences indicated on the right (in 10^{16} ions cm^{-2} units) at (a) 295 K and (b) 180 K.

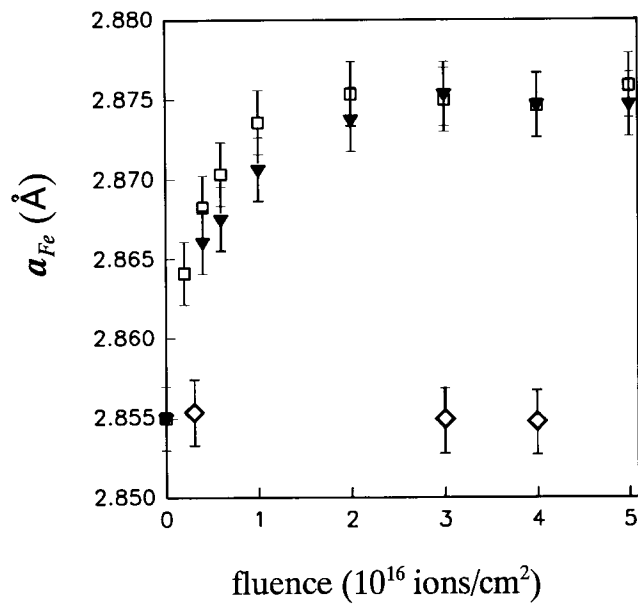


Figure 5. Fe layer lattice parameter as a function of fluence at 295 K (open squares), 180 K (solid down-triangles), and after annealing of samples irradiated at 295 K (open diamonds).

$(4Dt/\varphi)_{\text{ball}} = 0.22 \times 10^4 \text{ \AA}^4$. This underestimates our results at 180 K $(4Dt/\varphi)_{\text{exp}} = (0.64 \pm 0.06) \times 10^4 \text{ \AA}^4$ almost by three in spite of the fact that thermal effects are not important. This last hypothesis is reinforced by the Arrhenius plot of mixing efficiencies shown in figure 6 where no noticeable thermal dependence is observed up to 180 K. Chemical driving forces and temperature in the case of ballistic mixing are considered in the model developed by Traverse [2] for the case of regular solutions (rs) $((4Dt/\varphi) = (4Dt/\varphi)_{\text{ball}} + (4Dt/\varphi)_{\text{rs}})$. Even at low

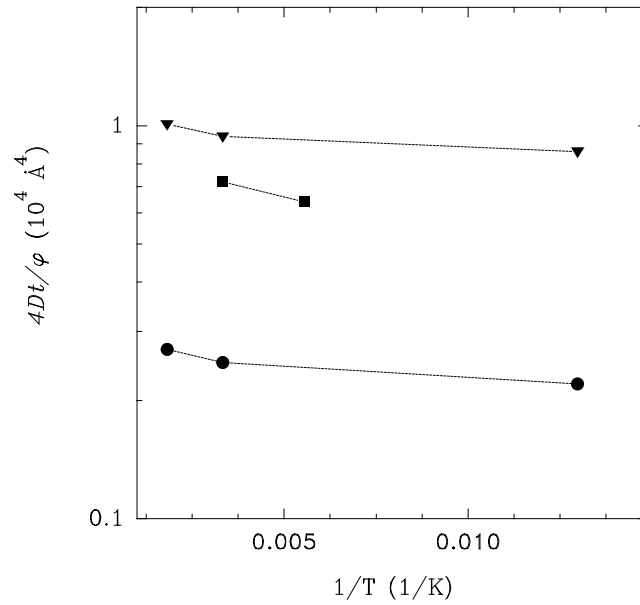


Figure 6. Thermal dependence of the mixing efficiency: present results (solid squares), after Ar-irradiation (solid circles), and after Xe ion-beam irradiation (solid down-triangles) taken from [6].

temperature, a reduction of the mixing rate should be expected due to chemical inter-diffusion leading to a negative contribution. The results of these calculations are evidence that collisional processes are not the only ones responsible for the observed behaviour.

Because of the magnitude of the deposited energy in the present experiment, $F_d = 115 \text{ eV } \text{Å}^{-1}$, the thermal spike models seem to be more adequate to interpret the experimental results. Calculations carried out using the model proposed by Johnson *et al* [8], where the mixing rate is proportional to F_d^2 , estimate a negative mixing rate $((4Dt/\varphi)_{ts} = -0.05 \times 10^4 \text{ Å}^4)$ using $\Delta H_m = +15 \text{ kJ mol}^{-1}$ [5] and $\Delta H_{coh} = -3.89 \text{ eV/at}$ [25], in discrepancy with calculations performed by Rauschenbach *et al* [6].

Models for mixing rate that take into account chemical driving forces in spatially separated [26] and cylindrical local spikes [27] suggest a linear relationship between the mixing efficiency and F_d . Unfortunately, numeric values of the two constants involved in the mixing rates expression are not available. However, extrapolating the reviewed experimental results [26, 27] to positive values of ΔH_m , a negative mixing rate might also be expected.

The above mentioned mixing processes alone or acting jointly are not able to explain the current results. The dependence of the mixing rate must be the result of the operation of other mechanisms.

To explain the enhancement of the solubility of one element into the other found in ball-milling experiments on Fe–Cu powders [28], it was assumed that the plastic deformation induces a change in the chemical potential [28]. This process could act as a driving force for alloying and mixing. Independent evidence of the extension of the solubility range in Cu/Fe multi-layers under ion-beam bombardment has been reported [10–12], where amorphous and quasi-crystalline solid solutions were observed. This hypothesis, based on an enhancement of solubility could also be applied to ion-beam mixing results of high positive heat of mixing. It may be able to account for the evolution of the Cu/Fe interface over the whole fluence range as well as the temperature dependence of the kinetics of mixing.

For fluence values corresponding to the mixing step, the observed Fe cell parameters are within those found for $\text{Fe}_x\text{Cu}_{1-x}$ solid solutions obtained by ball-milling from elemental Fe and Cu powders with the nominal composition $\text{Fe}_{90}\text{Cu}_{10}$ [28]; or from rapid quenching from the melt in the iron composition range 85 to 92.5 at.% [29]. However, the present lattice dimension changes cannot be explained as due to a solid solution formation since RBS results show that only a small portion of the layers are mixed.

The existence of internal stresses due to the defect structure and/or incorporation of Ar is supported by the evolution of the lattice parameter of the Fe layer with irradiation fluence (see figure 5). In addition, it has been established that dislocation structures are formed by Ar ion-implantation in pure Fe inducing plastic deformation [30]. This internal stress could modify the chemical potential, inducing a solubility enhancement, favouring mixing. Since the solubility enhancement displays an Arrhenius thermal behaviour, the decrease of the de-mixing and the increase of the mixing rate might also be interpreted in this way. Interstitial Ar ions and their associated damage in the unmixed region of the iron layer might cause the increase observed in the lattice spacing. This has been found to be the case for the behaviour of Pd/Fe bilayer systems mixed at room temperature with a 200 keV Kr^{2+} beam [10].

More recently, Nastasi *et al* [31], have advanced a similar explanation for their results on Ar ion-irradiation of multilayered DC sputtered thin films of TiN/B–C–N. They suggest a dependence of the chemical potential on the stress that allows them to obtain an analytical expression of $4Dt$ on the fluence. If applied to the present results, it is possible to think that in our case (figure 2) the change in the chemical potential would be revealed by an ‘incubation’ dose—that depends on the temperature at which the experiment is performed—that shifts the $4Dt$ values in the same sense as the predictions of their model.

5. Conclusions

The present ion-beam mixing results, explored in a wide fluence range, have allowed us to disclose a first step of de-mixing at low fluence values. The results of calculations using the well known models developed for miscible systems are not able to reproduce the present results quantitatively or qualitatively. Besides, hypotheses that could explain the experimental results in other immiscible systems are not of help to the interpretation of the behaviour of Fe/Cu interfaces under irradiation. The current results might be explained over the whole fluence range if it were assumed that the solubility is enhanced due to stress fields and plastic deformation induced by the incorporation of the Ar ions into the metal films.

Acknowledgments

Partial economic support by CONICET (PIP 4326 and PIA 7102), ANPCyT (PICT 1135 and 1277), CICPBA and Fundación Antorchas, Argentina, is gratefully acknowledged. JD, GP and RCM are members of Carrera del Investigador Científico, CONICET. GE is fellow of CONICET. The authors are indebted to Dr A Traverse for helpful discussions and for the RBS measurements using high-energy alpha particles. The x-ray diffraction analyses were carried out in the LANADI facilities at La Plata.

References

- [1] Desimoni J and Traverse A 1993 *Phys. Rev. B* **48** 13266
- [2] Traverse A 1988 *J. Less-Common Met.* **145** 451
- [3] Cheng Y T 1990 *Mater. Sci. Rep.* **5** 45

- [4] Miotello A and Kelly R 1992 *Surf. Sci.* **208** 340
- [5] de Boer F R, Boom R, Mattens W C M, Miedema A R and Niessen A K 1989 *Cohesion in Metals* (Amsterdam: North-Holland)
- [6] Rauschenbach B, Posselt M, Grötschel R, Brecht E, Linker G and Meyer O 1992 *Nucl. Instrum. Methods B* **69** 277
- [7] Sigmund P and Gras-Marti A 1981 *Nucl. Instrum. Methods* **182/183** 25
- [8] Johnson W L, Cheng Y T, Van Rossum M and Nicolet M A 1985 *Nucl. Instrum. Methods B* **7/8** 657
- [9] Patankar J, Phase D M, Kulkarni S A, Kulkarni V N, Ghaisas S V and Bhide Y G 1987 *Nucl. Instrum. Methods B* **19/20** 673
- [10] Principi G 1991 *Hyperfine Interact.* **66** 149
- [11] Gupta A, Principi G, Trotta P, Jannitti E, Tosello C, Gratton L M, Enso S, Lo Russo S and Rigato V 1992 *Surf. Coatings Technol.* **51** 429
- [12] Huang L J and Lin B X 1987 *Nucl. Instrum. Methods B* **18** 256
Huang L J, Liu B X and Li H D 1987 *Appl. Phys.* A44 269
Huang L J, Cheng M Q, Fan Y D, Li H D and Liu R X 1988 *J. Phys. F: Met. Phys.* **18** 269
- [13] Biersack J J P and Haggmark L G 1980 *Nucl. Instrum. Methods* **174** 257
- [14] Young R A, Skthivel A, Moss T S and Paiva-Santos C O 1994 *DBWS-9411. PC Program for Rietveld Analysis of X-ray Powder Diffraction Patterns* (Atlanta, GA: Georgia Institute of Technology)
- [15] March A 1932 *Z. Kristallogr.* **81** 285
Dollase G W A 1986 *J. Appl. Crystallogr.* **19** 267
- [16] Powder Diffraction Files of the Joint Committee on Powder Diffraction Data 1996 *X-Ray Powder Diffraction File Database* 23-224 (Swarthmore, PA: International Centre for Diffraction Data)
- [17] Sood D K, Bataglin G, Kulkarni V N, Lo Russo S and Mazzoldi P 1987 *Nucl. Instrum. Methods B* **19/20** 632
- [18] Averback R S, Peak D and Thompson J L 1985 *Appl. Phys.* A **38** 1
- [19] Averback R S, Okamoto P R, Baily A C and Stritzker B 1985 *Nucl. Instrum. Methods B* **7/8** 556
- [20] Jouen C, Delafond J, Junqua N and Goudeau P 1989 *Nucl. Instrum. Methods B* **43** 34
- [21] Hiller W, Buchgeister M, Eitner P, Koptzki K, Lilienthal V and Peiner E 1989 *Mater. Sci. Eng. A* **115** 151
- [22] Westendorp H, Wang Z L and Saris F W 1982 *Nucl. Instrum. Methods B* **194** 453
- [23] Crespo-Sosa A, Schaaf P, Bolse W and Lieb K P 1986 *Phys. Rev. B* **53** 14795
- [24] Averback R S, Peak D and Thompson J L 1986 *Appl. Phys.* A **39** 59
- [25] Kittel C 1976 *Introduction to Solid State Physics* (New York: Wiley)
- [26] Borghensen P, Liliendfeld D A and Msaad H 1991 *Nucl. Instrum. Methods B* **59/60** 563
- [27] Bolse W 1993 *Nucl. Instrum. Methods B* **80/81** 137
- [28] Eckert J, Holzer J C, Krill C E III and Johnson W L 1993 *J. Appl. Phys.* **73** 2794
- [29] Klement W Jr 1965 *Trans. Met. Soc. AIME* **233** 1180
- [30] Didenko A N, Kozlov E V, Sharkeev Y P, Tailashev A S, Rjabchikov A I, Pranjavichus L and Augulis L 1993 *Surf. Coatings Technol.* **56** 97
- [31] Nastasi M, Fayeulle S, Lu Y C, Kung H 1998 *Mater. Sci. Eng. A* **253** 202