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Solid state amorphisation reaction in sputtered and evaporated Ni/Zr multilayer films

A Thomä†

Physikalisches Institut der Friedrich-Alexander-Universität Erlangen-Nürnberg,
Erwin-Rommel-Strasse 1, D-8520 Erlangen, Federal Republic of Germany

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Abstract. Ni/Zr multilayer films with single-layer thicknesses of a few hundred nanometres were prepared by electron beam evaporation and by DC magnetron sputtering. The films were subsequently annealed under high-vacuum conditions at temperatures between 570 and 640 K where the progress of the solid state amorphisation reaction was monitored by *in situ* measurements of the electrical conductivity. From these measurements the interdiffusion coefficient D was derived. The samples were characterised by x-ray diffraction with Cu $K\alpha_1$ radiation in Seemann–Bohlin geometry and Rutherford backscattering with 25 MeV ^{16}O ions. Analysis of x-ray diffraction patterns shows that the Zr layers of evaporated samples are under tensile stress, whereas those of sputtered samples are nearly unstrained or under a small compressive stress. In sputtered films, D is about an order of magnitude smaller than in comparable evaporated films which is interpreted as a result of the different stress states. These results agree with the interpretation of our recent irradiation experiment. A correlation between the Zr crystallite size and D is found such that D decreases with increasing crystallite size. X-ray patterns also indicate that the nucleation of the amorphous phase depends on the crystallographic orientation in the Zr layers.

1. Introduction

Not only have the surprising discoveries about amorphisation by a solid state reaction (Yeh *et al* 1983, Schwarz and Johnson 1983) and by mechanical alloying (Koch *et al* 1983) opened up new means of forming amorphous alloys, but also their importance lies in the gain of new insights into the nature of metastable and amorphous states of matter (for a review see, e.g., Johnson (1986, 1988) and Samwer (1988)).

Among many other systems, crystalline Ni and Zr react at temperatures around 300 °C, which are well below the crystallisation temperatures of their binary compounds, to form an amorphous alloy by an interdiffusion process (Clemens *et al* 1984). Although the thermodynamic prerequisites and kinetic constraints, i.e. a large negative heat of mixing of the constituents and a sufficiently high mobility of only one species at the reaction temperature, for this process are understood in principle, a number of questions, such as the dependence of the reaction on the microstructure of the original layers or on strain fields, have not been answered satisfactorily. A further topic of interest is the nucleation of the glassy phase in the very early stage of the reaction.

† Present address: Fichtel & Sachs AG, Postfach 1423, D-8720 Schweinfurt, Federal Republic of Germany.

As a contribution to this field we have prepared Ni/Zr multilayered films by two different methods, namely thermal evaporation and sputtering, to produce films with different microstructures. It is well known that thin metal films condensed at temperatures small compared with their melting point exhibit tensile stress (see, e.g., Kienel 1987). The situation with sputtering is somewhat more complicated than with thermal evaporation. During sputtering, the pressure of the working gas can be used to induce compressive as well as tensile stress in thin films. For low working gas pressure films under compressive stress can be prepared (Thornton 1975, Thornton and Hoffman 1985). In a former experiment (Thomä *et al* 1988) a partial relaxation of tensile stress in evaporated Ni/Zr multilayers has been achieved by heavy-ion irradiation *prior* to annealing. The irradiated parts of the films have shown a deceleration of the solid state reaction. It is now of interest to compare films in which prior to the reaction strain fields with different signs prevail.

2. Experimental details

The evaporated samples were prepared from Ni and Zr ingots with a variable-beam electron gun onto water-cooled single-crystal sapphire substrates. The background pressure during evaporation was below 5×10^{-6} Pa. The samples consisted of 13–17 alternating layers of Ni and Zr, respectively, with single-layer thicknesses between 20 and 70 nm so that the overall thickness of the multilayer films was 0.6–1.0 μm . The overall Ni concentration was 0.56 or 0.67, respectively, at complete homogenisation of the film.

Samples were also prepared by DC magnetron sputtering in a three-cathode UHV chamber. In this case, only two of the cathodes were used for the two elements. Each cathode was alternatively covered with a suitable shutter to obtain the desired multilayer structure. The vacuum prior to sputtering was 3×10^{-6} Pa or better. Pure (99.9999%) Ar was used as a working gas. The sputtering gas pressure was kept at 0.3 Pa, which was the lowest pressure under which the plasma discharge could be stabilised. The films consisted of ten single layers of Zr with a thickness of 34 nm. The thickness of the corresponding Ni layers was systematically varied to obtain overall Ni concentrations between 0.35 and 0.70. Again, water-cooled single-crystal sapphire substrates were used.

In both cases the multilayers were prepared with a suitable evaporation mask, which gives the advantage of a well defined sample geometry, facilitating resistivity measurements. For reasons of symmetry the bottom and top layers always consisted of Ni with only half the normal thickness.

Exact knowledge of the layer thicknesses is of crucial importance for a quantitative analysis of the data, i.e. determination of diffusion coefficients. Therefore the film thickness was measured by an optical interference method, by an α -stepper as well as by Rutherford backscattering (RBS) (Chu *et al* 1978). The results of these methods agree within 10%. The RBS investigations were carried out with 25 MeV ^{16}O ions from the Erlangen tandem accelerator (Müller and Ischenko 1976).

Annealing experiments were performed under a vacuum of better than 5×10^{-5} Pa at temperatures between 570 and 640 K. The temperature varied less than 2 K during annealing and was controlled by a thermocouple. The amorphisation process was monitored by *in situ* measurements of the electrical conductivity parallel to the substrate.

The samples were characterised by x-ray diffraction in Seemann–Bohlin geometry using Cu $K\alpha_1$ radiation. This geometry is especially suited to thin-film studies (Feder and Berry 1970).

3. Results

A typical example of an x-ray pattern of an evaporated film in various states of the solid state reaction is shown in figure 1. For the as-prepared sample (figure 1, curve A), only the diffraction lines of face-centred cubic Ni and hexagonal Zr are visible. The strong enhancement of the Zr(002) and Ni(111) reflection indicates a preferential growth of the layers along the respective close-packed crystal planes. Annealing drastically reduces the crystalline lines and a broad maximum appears between them, which is characteristic for the newly formed amorphous Ni_xZr_{1-x} alloy. After an additional anneal at higher temperatures (figure 1, curve C) all Zr is consumed, but some Ni remains unreacted. The overall Ni concentration x of this sample is 0.67. There is an indication of a shift of the position of the Zr(100) reflection during the reaction.

An RBS spectrum of a sample before annealing (sample 32A) is displayed as the lowest spectrum in figure 2. In this experiment the sample was tilted 70° with respect to the incoming ion beam to enhance the depth resolution. From the six Zr layers the uppermost four are distinguishable on the high-energy side of the spectrum. Also, counting from the low-energy side, three of the seven Ni layers can be located. In the middle of the spectrum the signals from the upper Ni and lower-lying Zr layers overlap. A complete separation of the maxima due to Ni is not possible because of the straggling of the outgoing beam. The fact that the signal does not go back to zero between the upperlying Zr layers is not due to an intermixing of the layers even before annealing but reflects the high resolution which can be achieved using ^{16}O as a projectile. In this way, the isotopes of Zr can be separated, which is seen on the structure on the right-hand side of the first Zr signal. This was verified by a RBS computer simulation.

The effect of heat treatment on the samples is shown by the spectra for samples 32D and 32B, respectively. These samples were prepared simultaneously with sample 32A and in equivalent positions. As seen for sample 32B, the Ni concentration gradients, contrary to Zr, have already nearly vanished. Other workers (Cheng *et al* 1985) have shown that Ni is indeed the dominant moving species. The sharp maximum at about 9 MeV for sample 32B stems from the top layer of Ni, which therefore obviously does not take part in the reaction. This spectrum directly corresponds to the x-ray pattern in figure 1, curve C, for the same sample. Thus, the remaining crystalline reflections mainly come from the unreacted top layer.

The conductivity σ of the samples normalised to the value σ_0 at the beginning of the anneal is plotted versus the square root of the annealing time in figure 3. The initial linear part of the curves reflects the commonly observed (see, e.g., Samwer 1988) diffusion-limited growth of the amorphous phase. According to a model described by Schultz (1987) the interdiffusion coefficient D can be derived from the slopes of the straight lines if one assumes that the metallic layers of the films form a network of parallel conductors and a planar growth of the amorphous phase. The latter assumption is well documented by transmission electron micrographs (see, e.g., Schröder *et al* 1985). The values of D lie around $1 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$ at a temperature of 580 K (see below), which seems reasonable for diffusion in an amorphous alloy.

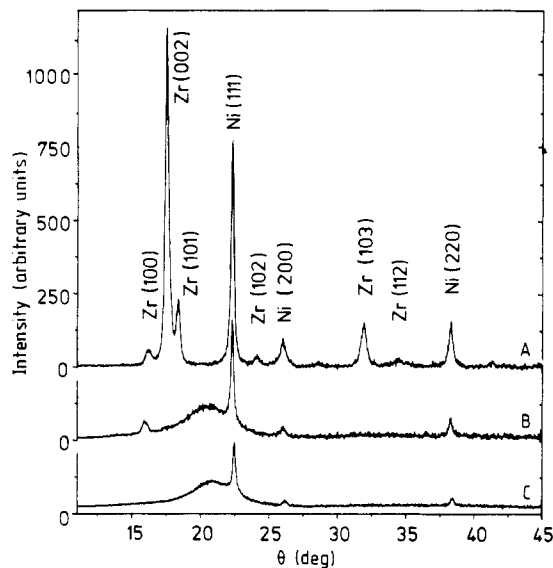


Figure 1. X-ray diffraction patterns of the evaporated sample 32B: curve A, after preparation; curve B, after 160 min at 600 K; curve C, after an additional 137 min at 622 K.

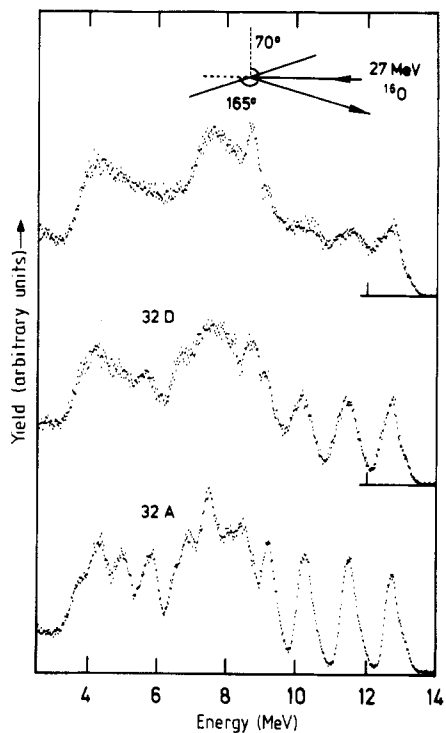


Figure 2. RBS spectra of three simultaneously prepared samples which were subjected to different heat treatments. Sample 32A is unannealed; sample 32D was annealed for 30 min at 585 K; sample 32B, was the same sample as for figure 1, curve C. The scattering geometry is drawn schematically in the figure.

An interesting feature of the diffraction patterns of nearly all annealed samples is that the Zr(100) reflection vanishes more slowly than the Zr(002) line although the latter is more prominent owing to the already-mentioned texture. This is shown in figure 4 for sputtered films of various compositions after the heat treatment given in the caption and compares well with figure 1, curve B, where the large Zr(002) line has already vanished but the much less intense Zr(100) reflection is still clearly visible. Remnants of Ni peaks are barely visible. For increasing Ni concentration the position of the first amorphous maximum is slightly shifted to higher diffraction angles θ . This can be understood since Ni is the smaller atom and therefore the average interatomic distance corresponding to the peak position gets smaller upon increasing the Ni content of the amorphous phase. If one assumes that amorphous $\text{Ni}_x\text{Zr}_{1-x}$ alloys prepared by rapid quenching and solid state reaction yield identical x-ray patterns, one can estimate the Ni concentration of the amorphous phase formed by annealing by comparison with data on melt-spun ribbons (Buschow 1984). Thus, amorphous phases with x between 0.48 and 0.67 are observed.

For the sputtered samples in the as-prepared state the mean crystallite size L_{Zr} of Zr as derived from the Scherrer formula (Cullity 1978) varies between 15 and 25 nm, which

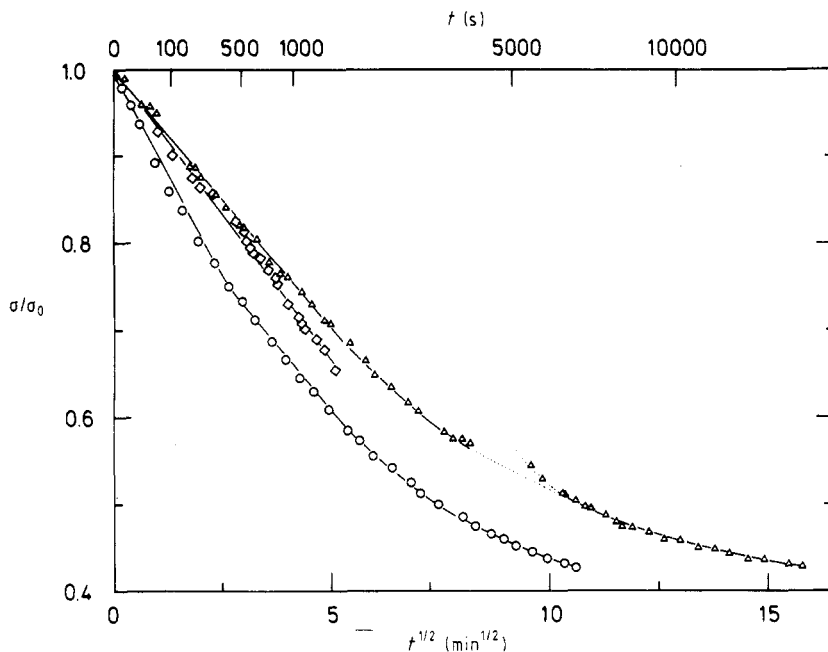


Figure 3. Electrical conductivity of some samples normalised to the value σ_0 at the beginning of the heat treatment plotted versus the square root of the reaction time: \circ , sample 32B, $T = 600$ K; \triangle , sample 32C, $T = 585$ K; \diamond , sample 32D, $T = 585$ K. The straight lines are least-squares fits.

is ascribed to a slightly varying thermal contact of the substrate with the water-cooled sample holder.

4. Discussion

A wealth of information can be extracted from the x-ray data. The composition of the initially formed amorphous phase is approximately $\text{Ni}_{0.55}\text{Zr}_{0.45}$ in close agreement with a recently published calculation of the free enthalpies of the involved phases (Bormann *et al* 1988) and an experimental result obtained by Schultz (1987) on Ni/Zr wires. According to the former work the maximum gain in free enthalpy upon forming the amorphous phase should be at a Ni concentration x of 0.56. The observed concentrations of amorphous $\text{Ni}_x\text{Zr}_{1-x}$ lie between $x = 0.48$ and $x = 0.67$, giving a lower bound for the glass-forming range. The glass-forming range for corresponding mechanically alloyed samples is much wider, i.e. from $x = 0.27$ (Schultz *et al* 1987, Thomä *et al* 1987) to $x = 0.83$ (Eckert *et al* 1988). There should be no fundamental reason for a difference between the glass-forming ranges of solid-state-reacted and mechanically alloyed samples because both processes can be explained by the same thermodynamical considerations. During mechanical alloying, the interdiffusion process is promoted by the severe mechanical deformations and the successive intermixing of the powder particles. On the other hand, the interdiffusion of the layers in thin film amorphisation is progressively slowed

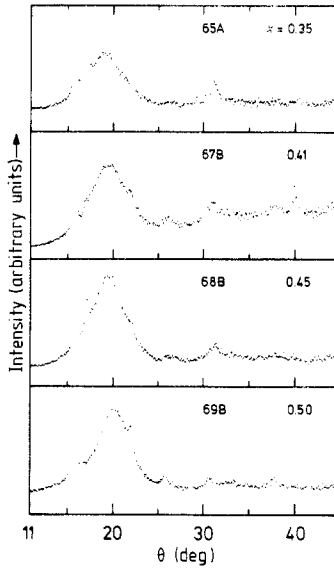


Figure 4. X-ray patterns of sputtered films after a heat treatment of 140 min at 581 K and 160 min at 608 K. The overall Ni content after an assumed complete homogenisation is given in the figure and increases from top to bottom.

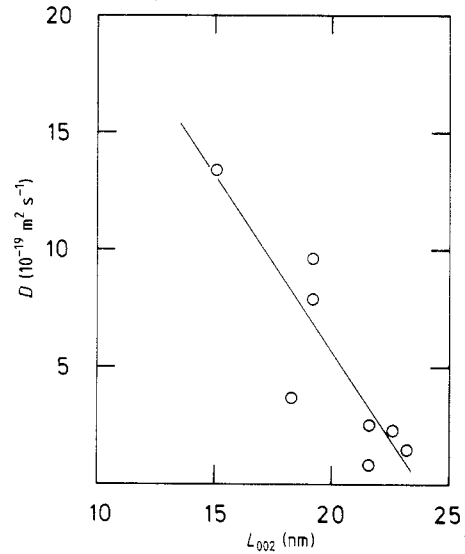


Figure 5. Diffusion coefficient D plotted versus the mean crystallite size L of Zr.

down by the growing amorphous layers which the species have to traverse to form new glassy material.

The delay in the amorphisation of the Zr(100) crystallites can also be seen in studies of the solid state reaction in transition-metal Zr diffusion systems published by other workers (see, e.g., Unruh *et al* 1985, Krebs and Samwer 1986). A time-determining step of the reaction is the diffusion through the newly formed amorphous interlayer. This does not depend on crystallite orientation. Thus, one arrives at the conclusion that already the first step of the reaction, i.e. nucleation of the amorphous phase, has to depend on how the Zr crystallites are oriented relative to the Ni concentration gradient. In our scattering geometry both the Zr(100) and the Zr(002) planes which are detected by the x-ray method lie nearly parallel to the Ni-Zr interfaces. However, the conclusion that the nucleation of the amorphous phase depends on the crystallographic orientation is in contradiction to the commonly accepted planar growth of this material (Schröder *et al* 1985). It could be tested by a study of the solid state reaction between Ni evaporated on different epitaxial Zr films.

In a recent publication (Thomä *et al* 1988) the changes in the Zr lattice spacings were studied for evaporated Ni-Zr multilayer films. It was observed that the lattice spacings of both the (100) and the (002) planes, d_{100} and d_{002} , respectively, deviate significantly from their bulk values because of tensile stresses in the films. In extreme cases they cause the films to peel off from the substrate. These stresses promote the solid state reaction and are released during the reaction. The relaxation of these stresses by heavy-ion irradiation *before* annealing leads to a deceleration of the reaction.

No sputtered sample was observed to peel off from the substrate. On the contrary, evaluation of $d_{(002)}$ and $d_{(100)}$ gives values lying in the range between 0.258 nm and 0.279 nm,

respectively, before annealing. This means that the sputtered films in the as-deposited state are nearly unstrained or even under a small compressive stress. After solid state reaction, values of d_{002} greater than 0.26 nm and of d_{100} greater than 0.282 nm are observed. Thus, in the course of the amorphisation, additional compressive stress builds up. For three samples this led to a bubbling of the layers, indicating a relaxation of the compression. Nearly the exact bulk value of d_{100} of these samples was then measured. The strain distribution is more easily detected in the Zr layers because Zr has a lower bulk modulus than Ni and therefore a less rigid lattice.

A common feature of the solid state reaction in both types of sample is therefore an enhancement of the Zr lattice spacings interpreted as a build-up of compressive stress. We speculate that this can be attributed to a relaxation effect in the newly formed amorphous layers due to the thermal annealing. Thus the initial amorphous material possibly consists of an unrelaxed open structure which may shrink during annealing.

Before one can compare the interdiffusion coefficient in evaporated and sputtered films, one has to consider an additional influence on D . In figure 5 a correlation between D and the mean size L_{002} of the Zr crystallites as evaluated for the (002) reflection is shown. With L_{002} increasing from 15 to 25 nm, as mentioned above, D falls off by an order of magnitude. All samples were annealed under nominally identical conditions. Experimental errors manifest themselves in the scatter of the data points but cannot account for the observed correlation. In the limit of indefinitely large crystals the result is in agreement with the findings of single-crystal experiments (Vredenberg *et al* 1986, Meng *et al* 1988). It supports the idea that grain boundaries are essential for the formation of the amorphous phase in the sense that they already contain disordered material. On the other hand, one can argue that in the layers with smaller grain size L_{002} a greater amount of grain boundary diffusion has taken place before the actual amorphisation reaction. Then the effective interface between Ni and Zr is enhanced, leading to erroneous evaluation of D . Also, it is questionable whether the evaluation of D remains correct in this case, because the basic assumption of the planar growth might no longer be valid.

Together with a compilation of data from the literature the Arrhenius plot (figure 6) shows the values for the interdiffusion coefficient D obtained in this study. The scatter of the data points for the sputtered samples reflects the dependence on L_{002} . The straight line is a least-squares fit for the temperature dependence of the evaporated samples. A value of 1.7 eV is obtained for the activation enthalpy of diffusion Q . Although the study covers only a very restricted range of temperatures a reasonable value for Q results. This in turn shows the reliability of the data evaluation. Since L_{002} of the evaporated samples is nearly constant at 30 nm, D of corresponding sputtered multilayers is an order of magnitude smaller. In agreement with the results of the irradiation experiment (Thomä *et al* 1988) this significant difference originates from the initial strain distribution in both types of sample.

5. Summary and conclusions

By comparison of the solid state interdiffusion reaction in Ni-Zr multilayers with different microstructures the influence of mechanical stress on this process could be qualitatively resolved. Whereas evaporated samples are under tensile stress, sputtered films are nearly unstrained.

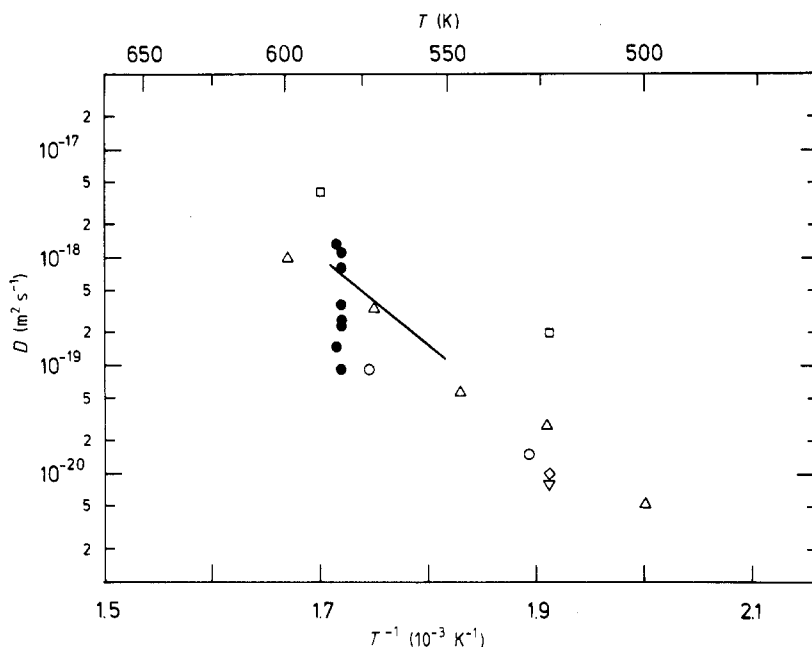


Figure 6. Logarithmic plot of the diffusion coefficient D over the inverse temperature (Arrhenius plot): ●, this work (sputtered); —, temperature dependence observed for evaporated samples. Data are taken also from the following references: □, Unruh *et al* (1985); △, Schultz (1987); ○, Hahn *et al* (1986); ⊗, Hahn *et al* (1986) (Ni tracer); ▽, Highmore *et al* (1987); ◇, Barbour (1985).

Furthermore, by means of heavy-ion irradiation of the *unreacted* evaporated samples an intermediate stress state could be achieved (Thomä *et al* 1988). In all types of sample, compressive stress builds up during the amorphisation and adds to the initial preparation-induced stress. This is presumably due to relaxation effects in the amorphous layer during the heat treatment. An alternative explanation would be the formation of Kirkendall voids as observed by other workers (Schultz 1984, 1985, Schröder *et al* 1985, Newcomb and Tu 1986). The speed of the diffusion process progressively slows down if the tensile stress of the layers is released, going from evaporated to irradiated and finally sputtered samples. A quantitative description of this behaviour is lacking owing to an incomplete understanding of diffusion in amorphous materials. However, it seems vividly clear that tensile stress parallel to the substrate enhances the average interatomic spacings above their usual values, which in turn results in an enhancement of the diffusivity perpendicular to the substrate.

Interesting hints concerning the formation of the amorphous phase have been found. As in many other studies, the Zr(100) reflection is observed to be more slowly affected by the amorphisation reaction than other crystalline Bragg peaks of Zr. This was interpreted as a dependence of the nucleation of the amorphous phase on crystallite orientation. Furthermore a surprising correlation between the diffusion coefficient D and the mean crystallite size L_{002} was found. This points to the importance of grain boundaries for the course of the reaction. The derivation of D , however, is based on the assumption of a planar growth of the amorphous phase. If this assumption is not justified, the correlation in figure 5 may be an artefact.

Both of the above observations thus lead to contradictions to the commonly accepted model of planar growth. It remains an open question to resolve this contradiction.

Acknowledgments

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References

- Barbour J C 1985 *Phys. Rev. Lett.* **55** 2872
- Bormann R, Gärtner F, Zöltzer K and Busch R 1988 *J. Less-Common Met.* **145** 19
- Buschow K H J 1984 *J. Phys. F: Met. Phys.* **14** 593
- Cheng Y T, Johnson W L and Nicolet M A 1985 *Appl. Phys. Lett.* **47** 800
- Chu W K, Mayer J W and Nicolet M A 1978 *Backscattering Spectrometry* (Orlando, FL: Academic)
- Clemens B M, Johnson W L and Schwarz R B 1984 *J. Non-Cryst. Solids* **61**–2 817
- Cullity B D 1978 *Elements of X-Ray Diffraction* 2nd edn (Reading, MA: Addison-Wesley)
- Eckert J, Schultz L, Hellstern E and Urban K 1988 *J. Appl. Phys.* **64** 3224
- Feder R and Berry B S 1970 *J. Appl. Crystallogr.* **3** 372
- Hahn H, Averbach R S and Rothman S J 1986 *Phys. Rev. B* **33** 8825
- Highmore R J, Evetts J E, Greer A L and Somekh R E 1987 *Appl. Phys. Lett.* **50** 566
- Johnson W L 1986 *Prog. Mater. Sci.* **30** 287
- 1988 *Mater. Sci. Eng.* **97** 1
- Kienel G 1987 *Dünnschichttechnologie* ed H Frey and G Kienel (Düsseldorf: VDI-Verlag) p 176ff
- Koch C C, Cavin O B, McKamey C G and Scarbrough J O 1983 *Appl. Phys. Lett.* **43** 1017
- Krebs H U and Samwer K 1986 *Europhys. Lett.* **2** 141
- Meng W J, Nieh C W, Ma E, Fultz B and Johnson W L 1988 *Mater. Sci. Eng.* **93** 87
- Müller P and Ischenko G 1976 *J. Appl. Phys.* **47** 2811
- Newcomb S B and Tu K N 1986 *Appl. Phys. Lett.* **48** 1436
- Samwer K 1988 *Phys. Rep.* **161** 1
- Schröder H, Samwer K and Köster U 1985 *Phys. Rev. Lett.* **54** 197
- Schultz L 1984 *Proc. Materials Research Society Eur. Meet. on Amorphous Metals and Non-Equilibrium Processing* ed M von Allmen (Les Ulis: Les Editions des Physique) p 135
- 1985 *Proc. 5th Int. Conf. on Rapidly Quenched Metals* ed S Steeb and H Warlimont (Amsterdam: North-Holland) p 1585
- 1987 *Science and Technology of Rapidly Quenched Alloys (Mater. Res. Soc. Symp. Proc. vol 80)* ed M Tenhover, L E Tanner and W L Johnson (Pittsburgh, PA: Materials Research Society) p 97
- Schultz L, Hellstern E and Thomä A 1987 *Europhys. Lett.* **3** 921
- Schwarz R B and Johnson W L 1983 *Phys. Rev. Lett.* **51** 415
- Thomä A, Adrian H and Saemann-Ischenko G 1988 *J. Less-Common Met.* **145** 115
- Thomä A, Saemann-Ischenko G, Schultz L and Hellstern E 1987 *Japan. J. Appl. Phys.* **26** 977
- Thornton J A 1975 *J. Vac. Sci. Technol.* **12** 830
- Thornton J A and Hoffman D W 1985 *J. Vac. Sci. Technol. A* **3** 576
- Unruh K M, Meng W J, Johnson W L, Thakoor A P and Khanna S K 1985 *Layered Structures, Epitaxy and Interfaces (Mater. Res. Soc. Symp. Proc. vol 37)* ed J H Gibson and L R Dawson (Pittsburgh, PA: Materials Research Society) p 551
- Vredenberg A M, Westendorp J F M, Saris F W, van der Pers N M and de Keijser Th H 1986 *J. Mater. Res.* **1** 774
- Yeh X L, Samwer K and Johnson W L 1983 *Appl. Phys. Lett.* **42** 242