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## THIN FILMS AND INTERFACES

### SELF-DIFFUSION IN $^{57}\text{Fe}/^{\text{nat}}\text{Fe}$ MULTILAYERS BY *IN-SITU* NEUTRON REFLECTOMETRY

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**Abstract** – In-situ time-of-flight neutron reflectometry on  $\text{Si}/[^{57}\text{Fe}(x \text{ nm})/^{\text{nat}}\text{Fe}(x \text{ nm})]_4/\text{Pt}$  with  $x = 4$  and 8 nm multilayers during consecutive heat treatments at 423, 448, 473 and 498 K reveal an unexpected rearrangement of free volumes and an interface smoothing in the isotopic Fe multilayer below 473 K, before the regime of regular Bragg intensity decay starts. The bilayer period dependence of the diffusivities at  $\sim 500$  K does not follow predictions of Harrison's theory for the C-regime of diffusion.

*Keywords:* self diffusion, iron, grain boundary diffusion, neutron reflectometry, in-situ.

## INTRODUCTION

Diffusion along grain boundaries (GBs) is a key feature for application-oriented properties of nanocrystalline materials [1]. Due to their metastability and increased defect concentration the bulk diffusion coefficient is inappropriate to describe diffusion in thin films since atomic migration via grain boundaries, dislocations and free surfaces leads to orders of magnitude faster paths as compared to the bulk diffusivity [2].

Harrison's scheme lays out three different regimes of diffusion, A, B and C [3]. At low temperatures in type-C diffusion the length  $L_d = (2Dt)^{1/2} \ll \delta$ . Here,  $D$  denotes the volume diffusivity during an isothermal annealing time  $t$  and  $\delta$  the grain boundary diameter (typically 0.5 nm). At low enough temperature the volume diffusion is negligible compared to the GB diffusion, and the effective diffusion coefficient,  $D$  is related to the GB diffusivity  $D_{GB}$ , via the grain boundary density factor,  $D = D_{GB}(4\delta/d)$ . In this model one assumes columnar close packed grains with grain diameter  $d$  equal to the film thickness. In nanocrystalline metals GBs can be engineered by controlling the grain size, which, in a multilayer is limited by the layer thicknesses.

Self-diffusion measurements have been performed in a series of alloys, some of which are also iron based. Most of these studies have been done using radiotracer techniques, secondary ion mass spectroscopy (SIMS), Rutherford backscattering (RBS), Auger electron spectroscopy (AES) and lately using neutron reflectivity (NR) [Ref. 4-6 and references therein]. Grain size evolution is common during diffusion, which, in turn, affects GB diffusivity. In order to realize GB diffusion with no grain size variation, secondary factors affecting the grain size should be avoided and diffusion lengths much below the grain size should be applied. In the present case heat treatments were limited to absolute temperatures below 30% of the layer material's melting point,  $T_m$ , well below the bulk grain growth regime starting around 800K in Fe. Such studies can be performed on multilayer films using neutron reflectometry (NR) [e.g. 4-6] with near-atomic length scale precision. The diffusion length is identified as the increase of the interface width (roughness, interdiffusion length) which can be extracted from the specular NR. NR was demonstrated to measure nanometric diffusion length of 1 nm with a depth resolution of 0.1 nm and respective ultra-low diffusivities down to  $10^{-26} \text{ m}^2/\text{s}$ . Such small diffusion length may allow characterization of solids in non-

equilibrium states. The interface holds the key to the functionality (tunnel magnetoresistance, exchange bias, spin-orbit coupling, etc.) of multilayer heterostructures but local structure and chemical effects are difficult to separate. Therefore we focus on self-diffusion and make use of the isotope selectivity of NR. As a continuation of our recent *ex-situ* study [7], *in-situ* preliminary specular and off-specular neutron scattering studies are reported here on two  $^{57}\text{Fe}/^{nat}\text{Fe}$  isotopic multilayers to further explore grain-size-assisted self-diffusion. The respective neutron scattering length densities (SLDs) are  $2\times 10^{-6}\text{\AA}^{-2}$  and  $8\times 10^{-6}\text{\AA}^{-2}$ , which provides sufficient contrast.

## EXPERIMENTAL

With the Si substrate held at room temperature two [ $^{57}\text{Fe}(x\text{ nm})/^{nat}\text{Fe}(x\text{ nm})$ ] $_4$ /Pt(4 nm) isotopic multilayer samples were prepared on Si(100) by molecular beam epitaxy (MBE) at Wigner RCP Budapest at a base pressure of  $1.0\times 10^{-9}$  mbar with  $x = 4$ , and 8 nm. Pt was deposited to avoid Fe oxidation.

Grain rotations, grain growth and/or recrystallization may cause the film texture to sharpen or deteriorate further. Diffusion studies, particularly when it falls within the grain boundary regime (type-C), would therefore be dependent upon the evolution of grains. Neutron reflectivity is commonly measured *ex-situ* on multilayer samples annealed at high temperature and then quenched to ambient temperature. Such *ex-situ* treatment, like annealing, apart from contamination of films often leads to evolution of the grain growth and the orientation-distribution with elapsed time (also change in distribution has been observed during waiting time). These processes being a thermally activated ones, affect the film texture and thereby cause ambiguities in the derived diffusivities [8].

Time of flight (TOF) specular and off-specular neutron reflectivity was recorded on the REFSANS horizontal-sample instrument [9] of HZG at the FRM II reactor of TU Munich in a dedicated furnace for reflectometry at 423, 448, 473 and 498K consecutively, for retention times of 600 minutes at each temperature, without breaking the vacuum. To avoid sample movement during annealing, the samples were soft-clamped on a sample holder, which comprises two spring loaded sample clips (S-Clips) on either edge of the sample holder. Even if there was a change of sample position during the annealing process, it would not have affected the measurement in TOF mode.

Over 1100 specular TOF reflectograms per sample were recorded (every 120 seconds) in a momentum transfer along the surface normal  $q_z$  range of  $0.5 < q_z < 0.9\text{ nm}^{-1}$  ( $\Lambda = 8\text{ nm}$

sample) and  $0.25 < q_z < 0.50 \text{ nm}^{-1}$  ( $\Lambda = 16 \text{ nm}$  sample), respectively. Five off-specular reflectograms per sample per temperature were also collected.

Pulsed high flux neutron sources, like European spallation source (ESS) will offer suitable conditions and TOF technique for future in-situ reflectometry to study dynamics in solids within a single equilibrium sample environment.

## RESULTS AND DISCUSSION

As a result of regular diffusion mixing and corresponding fade-out of the scattering length density (SLD) contrast, the multilayer Bragg peak is expected to decay with retention time at a rate dependent on the annealing temperature. According to the experimental results shown in Fig. 1 this is not the case here at low temperatures. The regular diffusion (indicative of SLD mixing) starts only above 450 K. However, there are segments in the time/temperature plot of the reflectivity where the Bragg peak height even increases (by up to 40%). Moreover, the position of the Bragg-peak at lower temperatures exhibits a relatively abrupt (as high as 10%) shift towards higher  $q$ -values, then gradually relaxes in both samples to the Bragg peak positions near the preparation values. Note that no shift in the critical edges has been observed upon annealing for forty hours. Off-specular data are not shown here as they do not show any change, while the specular reflectivities show change.

This unexpected dual behavior of the Bragg position may only be explained by structural rearrangements of the free volumes in the multilayer at lower temperatures. The increase of the peak intensity with time and increasing temperature is an indication of some kind of interface smoothing / sharpening. Similarly unexpected low temperature behavior was found by Tiwari et al. [10] on multilayers of the fully miscible Cu/Ni system and even on  $^{\text{nat}}\text{Fe}/^{57}\text{Fe}$  (sputtered) multilayers.

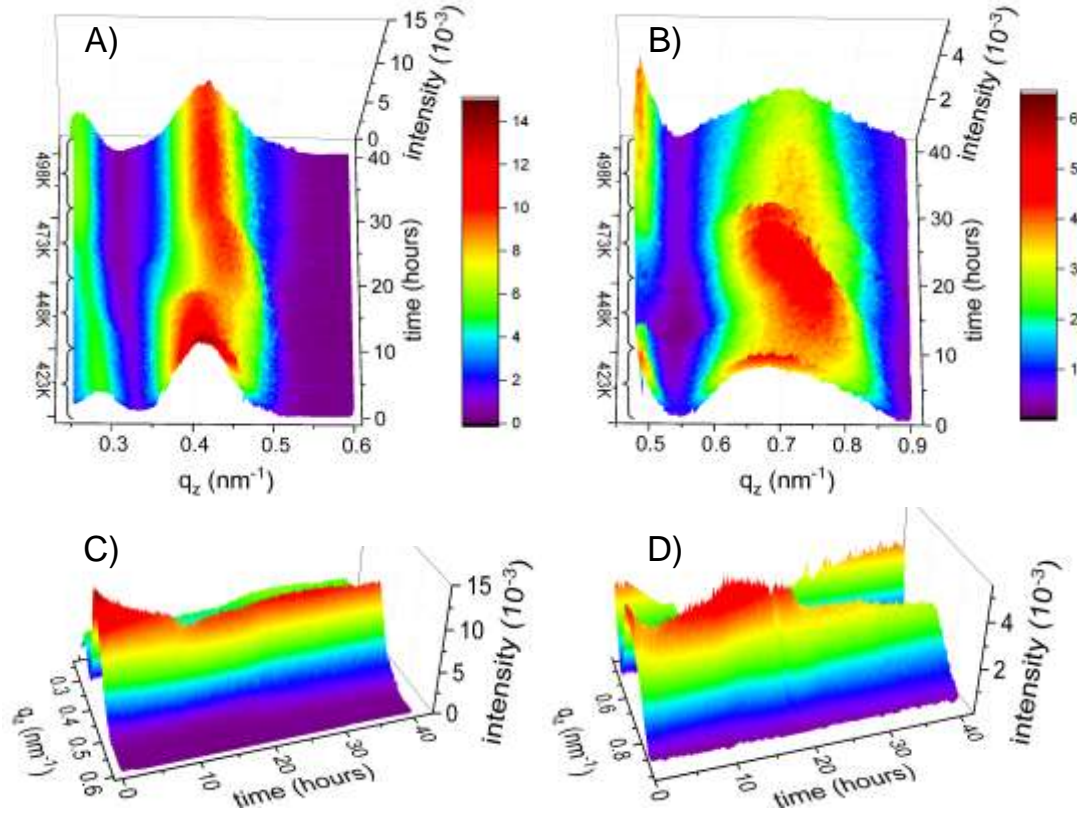


Figure 1 In-situ neutron reflectometry, intensity versus  $q_z$  and time, recorded on the REFSANS instrument at MLZ as a function of temperature and annealing time on  $\text{Si}(100)/[^{57}\text{Fe}(x \text{ nm})/^{nat}\text{Fe}(x \text{ nm})]_4/\text{Pt}(4 \text{ nm})$  multilayers with (A)  $x = 8$  and (B)  $x = 4$  nm. A single line of the 2D plot corresponds to data recorded for 120 seconds. (C, D) Shown below are the plots with a different perspective.

They interpreted their result by the role of exotic grain boundary structures (triple junctions), however, those could only be effective at extremely small grain size, i.e. in nanocrystalline materials. Structural rearrangement in sputtered films [11] is less surprising than in the principally more compact MBE-deposited ones since the neutral Ar sputtering gas may be freed at relatively low temperatures. The samples show high degree of texture and the typical grain sizes in our films with vertical dimensions of the size of layer thickness was reported earlier [12]. These results demonstrate that the interface behavior even in common multilayer systems is still at debate.

The intensity of the Bragg peak of order  $n$  of a periodic multilayer as a function of time  $t$  is

$$I_n(t) = I_n(0) \exp\left(-\frac{8\pi^2 n^2}{\Lambda^2} D(T)t\right), \quad (1)$$

where  $\Lambda$  is the bilayer period and  $D(T)$  is the effective diffusion coefficient at temperature  $T$  [6]. This exponential expression of the Bragg-peak intensity was fitted for the „regular” diffusion regions (see Fig 2).

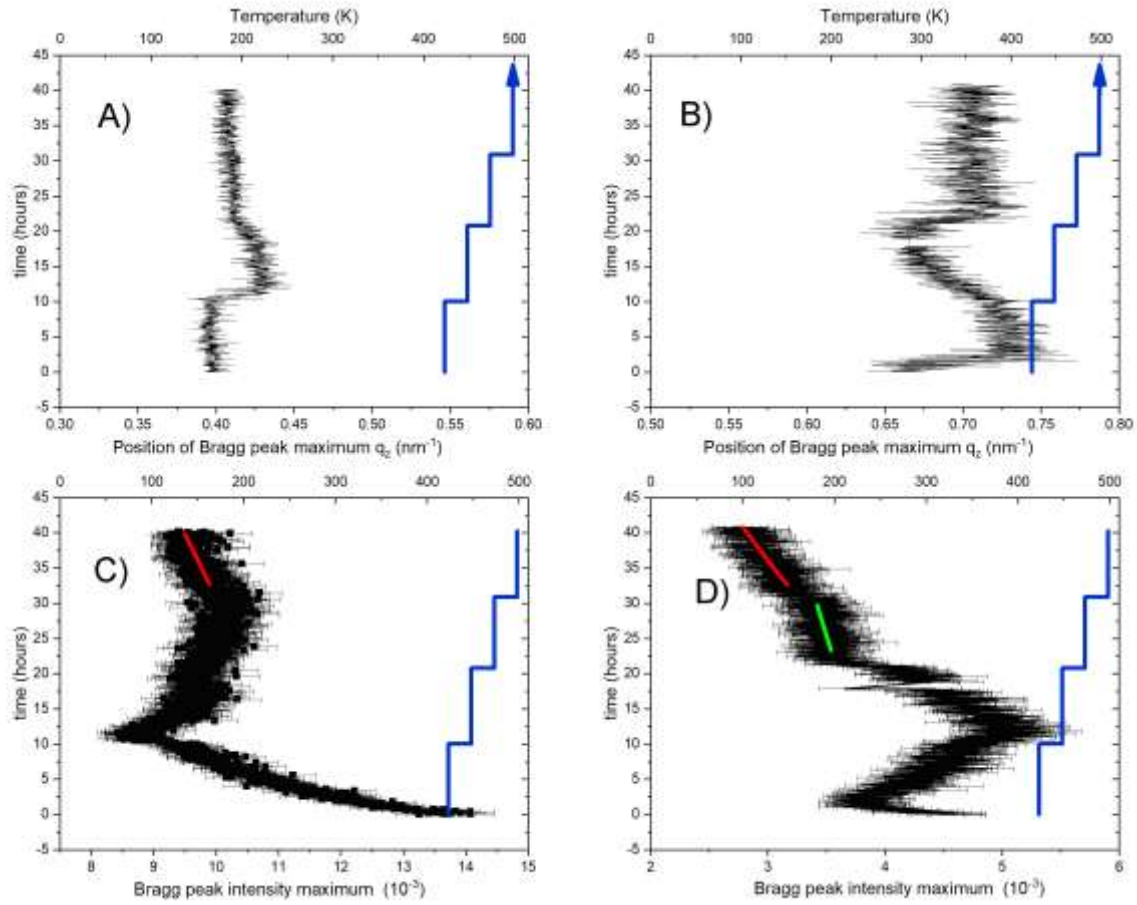


Figure 2. Time and temperature evolution of the neutron reflectivity Bragg peak positions (panels A) and B) and intensities (panels C) and D)) for Si(100)/<sup>57</sup>Fe( $x$  nm)/<sup>nat</sup>Fe( $x$  nm)]<sub>4</sub>/Pt(4 nm) multilayers,  $x = 8$  nm (A) and C)) and  $x = 4$  nm (B) and D). The temperatures and retention times are indicated by the blue lines. The peak intensity decay was fitted in the regular diffusion regimes (in red and green) and resulted in diffusivities displayed in Table 1.

The fit results are highlighted in red for the 498 K retention and in green for 473 K. The free parameters were  $I_n(0)$  and  $D(T)$ . The fitted  $D$  values and the corresponding diffusion lengths  $L_d = \sqrt{2 \cdot Dt}$  (for the 600 minutes retention time) are displayed in Table 1.

	$D(498 \text{ K}) [\text{\AA}^2/\text{s}]$	$L_d(498 \text{ K}) [\text{\AA}]$	$D(473 \text{ K}) [\text{\AA}^2/\text{s}]$	$L_d(473 \text{ K}) [\text{\AA}]$
$x = 4 \text{ nm}$	$3.5(\pm 0.3) \times 10^{-4}$	5.0	$1.2(\pm 0.3) \times 10^{-4}$	2.9
$x = 8 \text{ nm}$	$5.1(\pm 0.7) \times 10^{-4}$	6.1	–	–

Table 1. Derived diffusivities and diffusion lengths (for 600 mins retention time) for the investigated Si(100)/[<sup>57</sup>Fe(*x* nm)/<sup>nat</sup>Fe(*x* nm)]<sub>4</sub>/Pt(4nm) samples.

Assuming pure GB diffusion in both  $\Lambda = 8$  and 16 nm multilayers, one may test scaling of the diffusivity with the GB density factor. The grain size is limited by the multilayer period, and since  $D = D_{\text{GB}}(4\delta/d)$ , consequently  $D(\Lambda = 8 \text{ nm}) \approx 2 \cdot D(\Lambda = 16 \text{ nm})$  is expected from Harrison's theory for the C-regime. But for 498 K we experimentally derive:  $D(\Lambda = 8 \text{ nm}) \approx 0.69 \cdot D(\Lambda = 16 \text{ nm})$ , i.e. the diffusivity does not scale with the layer thickness according to Harrison's theory. As a consequence, the very prerequisite of studying GB diffusion without effects of concurring grain growth is likely to be hampered. Further studies are required to clarify the disagreement which will be taken up in the near future.

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