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Dynamics in submonolayer Fe-films

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Abstract

The properties of thin films are directly connected with the atomic structure. At elevated temperatures this structure is determined by atomic dynamics. Pronounced effects are expected for thin films of low coverage. We have investigated electronic and dynamical properties of a submonolayer Fe film on a W(1 1 0) substrate with nuclear resonance scattering (NRS) in grazing–incidence geometry. This atomistic technique is best suited for such investigations due to its element (isotopic) and submonolayer sensitivity as demonstrated in the model system of Fe/W(1 1 0). A simple relaxation model was used to explain the temperature dependence of the NRS spectra. The relaxation rates and diffusion coefficients have been calculated.
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1. Introduction

Fe on a W(1 1 0) substrate offers the opportunity to investigate the relationship between structure, hyperfine interactions and dynamics. By varying preparation conditions (deposition temperature, coverage, substrate miscut, annealing temperature) a variety of nanostructures with unique properties can be produced. The reason for these properties is an interplay of anisotropies, which are tightly connected with atomic structure and dynamics on atomic scale. The use of syn-chrotron radiation, in particular the technique of nuclear resonant scattering of synchrotron radiation (NRS) in grazing–incidence geometry, allows one to study simultaneously dynamics, structure and magnetic properties on this scale.

We chose a system consisting of a submonolayer of iron on a vicinal surface of tungsten to investigate the dynamics in the submonolayer using the NRS method. An iron monolayer on tungsten is a model system for pseudomorphic growth and is stable up to 1100 K as known from Auger electron spectroscopy (AES) measurements [1]. Therefore, high-temperature investigations are possible. The challenging feature of the experiment was to test the submonolayer sensitivity of the NRS method in grazing–incidence geometry and

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to perform studies of dynamics of an uncoated iron submonolayer.

2. Experimental details

The iron film was deposited using molecular beam epitaxy (MBE) at room temperature onto a vicinal tungsten substrate. The deviation of the surface normal of the substrate from the [1 1 0] direction results in atomic steps along the in-plane [0 0 1] direction. The density of the steps increases with deviation angle. The miscut angle of the substrate relative to the [1 1 0] direction was $6.3 \pm 0.1°$. The resulting terrace width of about 30 Å was confirmed by LEED measurements of a clean substrate and checked again after the deposition of a 0.6 ML of iron. The substrate was polished ex situ and cleaned in situ by multiple flashing up to 2300 K. Detailed preparation conditions and sample characterisation techniques are published in [2]. Before the measurement the sample was annealed at 370 K. We suppose that the deposited iron submonolayer consists of well separated pseudomorphic islands with monoatomic height similar to the sample investigated by Röhlsberger et al. [3].

To investigate the properties of a submonolayer of iron by nuclear resonant scattering three conditions have to be fulfilled: the geometry of grazing–incidence has to be used, a very strong source of well collimated radiation must be applied and the sample has to be produced and stored under UHV conditions. The measurements were performed at the ID18 beamline of ESRF using a typical set-up for NRS in grazing-incidence geometry. The synchrotron radiation was monochromised to an energy bandwidth of 6 meV and vertically focussed to 150 μm. The maximum of the delayed intensity was found at the incidence angle of 4.7 mrad. The total reflection angle of tungsten and iron for the used 14.4 keV radiation is 5.5 and 3.8 mrad, respectively. The direction of the incidence beam was parallel to the [0 0 1] direction of the substrate neglecting the small incidence angle. Details about the beamline set-up may be found in [4]. The sample was stored in a UHV high-temperature chamber dedicated to

synchrotron investigations in grazing–incidence geometry.

3. Experimental method

Nuclear resonant scattering (NRS) is a well established method to study structural and magnetic properties of materials as well as dynamics on an atomistic scale. This method combines the high brilliance of a third generation synchrotron source and the excellent characteristics of Mössbauer spectroscopy (MS). The unique feature of the NRS method, i.e. the selectivity for Mössbauer isotopes, was used to receive information on the dynamics in the submonolayer of iron in our experiment. The grazing–incidence geometry was used to enhance the signal from the iron layer. In this way even a submonolayer sensitivity can be reached as demonstrated in this work.

There are two features of NRS, which are exploited in this work:

- First, NRS is sensitive to the atomic jump diffusion mechanism in different measurement geometry (transmission [5,6], Bragg reflection [7], grazing–incidence [8]).
- Second, NRS is a technique for the investigation of hyperfine parameters, especially in thin films [9].

In this work the electric quadrupole interaction is of particular importance. An asymmetric electronic charge distribution around a nucleus leads to a splitting of its excited energy level. The incoming synchrotron radiation excites both energy levels, i.e. the radiation re-emitted by the nucleus consists of two waves with similar frequencies. Their interference determines the characteristic beat pattern in time. The relative orientation of the polarisation vector of the synchrotron radiation and the main axis of the EFG in the sample determines the shape of the spectra. The NRS spectrum of a thin sample with an energy state split due to quadrupole interaction is an exponential function if the main axis of the EFG is perpendicular to the polarisation vector and to the wave vector of the incoming synchrotron

radiation. The spectrum consists of a beat pattern if the EFG main axis is tilted out of this position [10,11].

4. Results and discussion

We have measured time spectra of a 0.6 ML iron layer on W(1 1 0) at various temperatures. The results are displayed in Figs. 1 and 2. In the temperature range RT – 670 K a reversible effect was observed. With increasing temperature the period of the beats also increases and at 670 K the beats disappear completely (Fig. 1). We proved the temperature reversibility of this effect checking the structural stability of the sample by taking a RT spectrum after each temperature step. The comparison of the first RT measurement and the RT measurements after the measurement at 670 K shows no difference (Fig. 2) proving, therefore, the reversibility of the effect.

The beat pattern and its development will be explained in the following.

Iron submonolayers on W(1 1 0) are known to be paramagnetic at RT with Curie temperatures in the temperature range 179 K [12]–210 K [13,14] for 0.8 ML thick films. Furthermore, an electric field gradient exists at the nuclear site due to the broken

Fig. 2. Comparison of the first room temperature measurement (□) and the RT measurement after the highest temperature 670 K (●). The shape of the spectrum remains without change after and between measurements at higher temperatures (Fig. 1). This is a proof of the temperature stability of the sample and the reversibility of the effect shown in Fig. 1. The dashed line demonstrates the natural decay of the excited energy state of the [57]Fe nucleus.

translational symmetry [13,15]. The Fe(1 1 0) monolayer film is an example for a film with an interplay of the out-of-plane anisotropy resulting from the perpendicular substrate-vacuum anisotropy, and the in-plane anisotropy due to the lower (twofold) local symmetry of the (1 1 0) plane. This interplay defines the position of the main axis of the EFG, i.e. the shape of the NRS spectrum. The expected direction of the EFG main axis for a perfect monolayer is perpendicular to the surface due to the broken translational symmetry at the surface. In this case the nuclear resonant spectrum should have the shape of a simple exponential decay due to the perpendicular orientation of the EFG main axis relative to the polarisation plane of the synchrotron radiation [10]. In our measurements a beat pattern corresponding to the main axis of the EFG tilted out of the direction perpendicular to the surface appeared. We conclude that the tilt of the EFG main axis is caused by the high fraction of iron atoms on the island edges in combination with the twofold symmetry in the (1 1 0) plane. The main axis of EFG is tilted about 60° from the surface normal. The measured value at room temperature for the main axis V_{zz} is $10(2) \times 10^{21}$ Vm^{-2} assuming an asymmetry parameter $\eta = 0$.
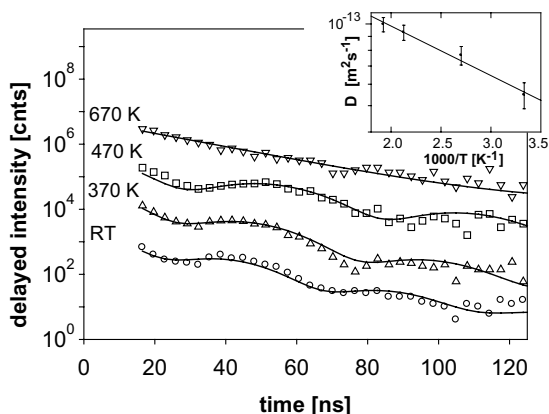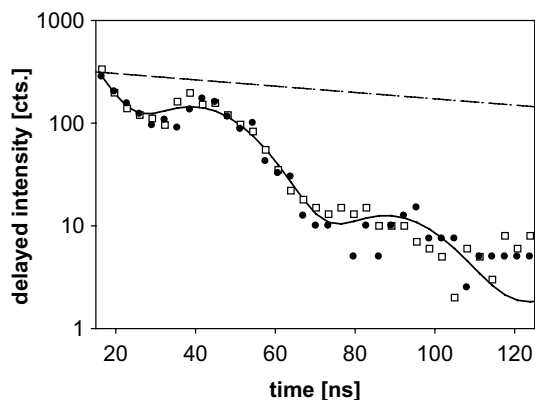

Fig. 1. A beat pattern corresponding to a quadrupole interaction is observed at RT. At 370 and 470 K a shift of the beats to larger time values is clearly visible. The beats disappear finally at 670 K. The spectra are shifted relatively to each other. The inset shows the diffusion coefficients D (m^2 s^{-1}) estimated from the increase of the beat period.

The temperature dependence can be explained as a relaxation effect caused by diffusion of iron atoms: diffusing atoms lead to a random fluctuation of the nearest neighbour arrangement, this causes fluctuations of hyperfine interactions and finally a "collapse" of the quadrupole splitting [16,17]. The result is a single Lorentzian line in the energy domain and an exponential decay in the time domain (Fig. 1, the spectrum at 670 K).

For the relaxation model of the quadrupole splitting Δ a simple approximation, with a linear relation between the quadrupole splitting and the relaxation rate ω was used:

$$\Delta(\omega) = \Delta_0 - 2\hbar\omega,$$

where Δ_0 is the quadrupole splitting at lowest measured temperature. The relaxation rates ω estimated from this relation for 300, 370, 470 and 520 K are $2.9(4)\times10^6$, $4.1(4)\times10^6$, $4.9(4)\times10^6$ and $5.3(4)\times10^6$ s^{-1}, respectively. Assuming that the relaxation frequency is similar to the jump frequency of atoms and for nearest-neighbour jumps the diffusion coefficient D can be calculated as

$$D = \frac{1}{4}\sum_{i=1}^{N} l_i^2 \omega$$

where l is the length of the jump vector, ω is the relaxation rate or jump frequency and N is the number of nearest neighbours. The resulting diffusion coefficients are $5.5(6)\times10^{-14}$, $7.7(6)\times10^{-14}$, $9.3(6)\times10^{-14}$ and $10.0(6)\times10^{-14}$ m^2 s^{-1}, respectively. Plotting this values into an Arrhenius plot results in the activation energy $E_A = (36 \pm 6)$ meV (Fig. 1 inset). Taking into account all systematic uncertainties contained in our model we estimate the value of the activation energy to be between 20 and 50 meV. One should mention that in this case the simplest possible relaxation model has been chosen. A more sophisticated model based on the theory of Tjon and Blume [16,17] can provide slightly different values of the activation energy.

Further investigations have to be done in order to receive more information about the morphology (STM, CEMS) of the iron submonolayer, however, the main experimental aim, i.e. to receive NRS spectra from an uncoated iron submonolayer was successfully achieved.

5. Conclusions

The investigation of structure and dynamics of the submonolayer film is possible using a synchrotron radiation source of third generation. The NRS spectra of an 0.6 iron ML on a vicinal W (1 1 0) show a beat pattern as a result of an electric field gradient tilted out of the direction perpendicular to the surface. The increase of the beat period with temperature is explained as a relaxation effect. A simple relaxation model leads to a relaxation rate, which is in the order of 10^6 s^{-1}. The diffusion coefficient, assuming a nearest neighbour jump length, is at room temperature $D = 5.5(6) \times 10^{-14}$ m^2 s^{-1}.

References

[1] U. Gradmann, G. Liu, H.J. Elmers, M. Przybylski, Hyperfine Interact. 57 (1990) 1845.
[2] J. Korecki, M. Kubik, N. Spiridis, T. Ślęzak, Acta Phys. Polonica A 97 (2000) 129.
[3] R. Röhlsberger, J. Bansmann, V. Senz, K.L. Jonas, A. Bettac, O. Leupold, R. Rüffer, E. Burkel, K.H. Meiwes-Broer, Phys. Rev. Lett. 86 (2001) 5597.
[4] R. Rüffer, A.I. Chumakov, Hyperfine Interact. 97–98 (1996) 589.
[5] B. Sepiol, A. Meyer, G. Vogl, R. Rüffer, A.I. Chumakov, A.Q.R. Baron, Phys. Rev. Lett. 76 (1996) 3220.
[6] B. Sepiol, A. Meyer, G. Vogl, H. Franz, R. Rüffer, Phys. Rev. B 57 (1998) 10433.
[7] H. Thiess, M. Kaisermayr, B. Sepiol, M. Sladecek, R. Rüffer, G. Vogl, Phys. Rev. B 64 (2001) 104305.
[8] M. Sladecek, B. Sepiol, M. Kaisermayr, J. Korecki, B. Handke, H. Thiess, O. Leupold, R. Rüffer, G. Vogl, Surf. Sci. 507–510C (2002) 124.
[9] R. Röhlsberger, J. Bansmann, V. Senz, K.L. Jonas, A. Bettac, K.H. Meweis-Broer, O. Leupold, Phys. Rev. B 67 (2003) 245412.

[10] H. Grünsteudel, V. Rusanov, H. Winkler, W. Meyer-Klaucke, A.X. Trautwein, Hyperfine Interact. 122 (1999) 345.

[11] G.V. Smirnov, Hyperfine Interact. 123–124 (1999) 31.

[12] J. Hauschild, H.J. Elmers, U. Gradmann, Phys. Rev. B 57 (1998) R677.

[13] M. Przybylski, Hyperfine Interact. 113 (1998) 135.

[14] M. Przybylski, U. Gradmann, Phys. Rev. Lett. 59 (1987) 1152.

[15] M. Przybylski, U. Gradmann, J. Appl. Phys. 63 (1988) 3652.

[16] J.A. Tjon, M. Blume, Phys. Rev. 165 (1968) 456.

[17] S. Dattagupta, K. Schroeder, Phys. Rev. B 35 (1987) 1525.