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# An IR-transmission spectroscopical study of the influence of substrate surface defects on the morphology and the electronic structure of ultrathin Fe grown on MgO(001)

Gerhard Fahsold*, Andreas Priebe, Norbert Magg, Annemarie Pucci

*Institut für Kirchhoff-Physik, Ruprecht-Karls-Universität Heidelberg, Albert-Ueberle-Strasse 3-5, D-69120 Heidelberg, Germany*

## Abstract

IR broad-band properties are sensitive to electronic transport and charge localization. This allows to investigate the electronic structure of ultrathin metal films by means of IR-transmission spectroscopy. As this electronic structure is determined by the interfaces of the film, the dynamic conductivity also reflects its morphology. We performed in-situ transmission spectroscopy in the middle infrared (MIR) during the evaporation of Fe on MgO(001) at room temperature in ultrahigh vacuum. We varied the quality of the substrate surface by using MgO(001) cleaved in air and cleaved in ultrahigh vacuum. The difference in the thicknesses for the onset of continuous transport properties of the growing films is well detected by their different IR-spectroscopical behavior. For continuous films, we calculate the thickness dependent scattering of electrons and the thickness dependent effective IR-optical oscillator strength from their IR-optical data. For MgO cleaved in air compared with cleavage in ultrahigh vacuum, the continuous thin film model becomes relevant at a smaller thickness, i.e. the substrate is covered faster in this case. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Infrared spectroscopy; Dynamic conductivity; Thin films; Classical size effect; Iron; MgO

## 1. Introduction

While IR-vibrational spectroscopy is known as a powerful tool to investigate atomic dynamics, IR broadband properties have gained less attraction. In the case of metals, these properties are a result of the charge transport and the dynamic electronic structure [1]. As morphology and interfaces influence electron scattering and electron localization, IR-spectroscopy is able to yield information on them. Furthermore, IR-optical properties of low-dimensional metal systems are of much relevance for the quantitative vibrational spectroscopy of adsorbates on these systems [2].

As, e.g. adsorbates show properties that depend on the size and the shape of low-dimensional systems [3], much effort is done to investigate and to control the morphology during growth of metallic ultrathin films. It is well known that growth parameters like substrate temperature and deposition rate influence the morphology of a growing film, but often, less attention is paid to the role of defects on the substrate surface. In the case of metal oxides with a high thermal and chemical stability, it is interesting, in which way the exposure to air will determine the development of a continuous metal film.

From our He-atom scattering studies we know that Fe grows on perfect MgO(001) as 3d islands before coalescence of these islands leads to a complete coverage of the substrate [4]. Compared with noble metal on ionic crystals (Ag/KBr, e.g.), this coverage occurs at relative low thickness. As it will come out of this paper, the exposure of the substrate surface to air helps to partially overcome the tendency towards 3d growth. We will report on IR-transmittance measurements and their interpretation for the substrate surface dependent growth and electronic structure, respectively, of Fe on MgO(001). In this study, we restrict our interpretation to the investigation of the onset of the continuous transport behavior.

## 2. IR-dynamical conductivity of continuous thin films

Optical properties of conductive matter depend on the relaxation of electrons and their effective mass [1,5], which both depend on the frequency of the external field [6]. In thin films, additional relaxation mechanisms lead to the classical size effect. They depend on surface geometry [7] and on surface roughness [8,9], and they are influenced by adsorbates [10–12]. Furthermore, the confinement of

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* Corresponding author. Fax: + 49-6221-549-262.

*E-mail address:* fahsold@urz.uni-heidelberg.de (G. Fahsold)

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electrons changes the density of states at Fermi level and the band structure related dynamic (optical) mass of the electrons. For real grown thin films, additional problems occurs due to irregular surfaces and interfaces and the relaxation and depolarization effects correlated to them.

In the following, we shortly explain our calculations. The basics of frequency dependent scattering in the MIR and the details will be given in another paper [13].

The Drude type dependency of the dielectric function $\varepsilon$ on material constants is given by

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p(\omega)^2}{\omega \cdot [\omega + i\omega_\tau(\omega)]} \tag{1}$$

where $\omega$ is the frequency of the external field and $\varepsilon_\infty$ stands for the background polarizability. As we are interested in metallic properties in the MIR, we use $\varepsilon_\infty = 1$ for calculations reported here. To account for true Fe bulk properties we use frequency dependent functions for the plasma frequency $\omega_p$ and for the inverse relaxation time $\omega_\tau$, which we derive from frequency dependent experimental data from bulk polycrystalline iron [14] by using the formal dependence of the dielectric function on $\omega_p$ and on $\omega_\tau$ (Eq. (1)). The resulting frequency dependencies fit into the common rough scheme of electron dynamics in metals. At room temperature and at IR frequencies the electron-phonon scattering dominates the electronic relaxation [15] and it introduces a frequency dependence to $\omega_p$ [6].

In thin films the surface and the interface with the substrate influence electronic relaxation. To consider this, usually a relaxation rate is introduced [16,17] which is added to the bulk rate

$$\omega_\tau^{\mathrm{TF}}(\omega, d) = \omega_\tau(\omega) + \alpha(d)\frac{v_F}{2d} \tag{2}$$

This surface scattering contribution scales with the average film thickness $d$ and with the velocity of the quasi-free electrons at Fermi-level $v_F = 1.98 \times 10^6$ m/s [5]. The factor of 1/2 is due to averaging over all directions with a positive component perpendicular to the film surface. The thickness dependent factor $\alpha$ plays a two-fold role. Originally, a probability proportional to $\alpha$ was used by Fuchs [16] to describe the non-specularity of the surface scattering. In our analysis, the roughness parameter $\alpha$ includes also the mesoscopic roughness of the film. Suppose, for instance, an isotropic electron gas and a film with perfectly parallel interfaces. In this case, $\alpha$ should equal unity as long as each collision with an interface is counted as a scattering out of specular. Now, for a heterogeneous film Namba [17,18] proposes to average the surface scattering over the mesoscopic lateral variation of the local thickness. In this treatment mesoscopic roughness appears as an increase in $\alpha$, which may go far above unity. Due to this sensitivity of $\alpha$ on morphology, the determination of this parameter as a function of $d$ supplies a tool for gaining insight into the microscopic atomic roughness of the interfaces and the mesoscopic morphology of the film. When calculating the thin film dielectric function, we take into consideration also a thickness dependent variation of $\omega_p(\omega)$ and therefore replace it in Eq. (1) by

$$\omega_p^{\mathrm{TF}}(\omega, \mathrm{d}) = \beta(d)\ \omega_p(\omega) \tag{3}$$

With this frequency independent scaling factor $\beta$ we may account for quantum size effects [19] and also for depolarization effects in films with non-flat surfaces [20].

Beyond certain limits due to island structure or localization we expect a failure of the above described model. Metal films which incompletely cover the insulating substrate cannot be described with a finite $\alpha$. But also for films thicker than the mean free path $\lambda_{\mathrm{MFP}}$ of electrons in bulk material ( $\sim$ 5 nm at 2000 $\mathrm{cm}^{-1}$ as calculated from the data in Ref. [14]), we expect a less good description of experimental results as the scattering of electrons is treated irrespective of their distances to the film boundaries. A fully quantum mechanical treatment of the transport properties is preferred either if the additional scattering in the thin film leads to a $\lambda_{\mathrm{MFP}}$ equal to or smaller than the Fermi-wavelength $\lambda_F$ (0.37 nm in bulk-Fe [5]), or if $d^2 < \lambda_{\mathrm{MFP}}\lambda_F$. [8]. Due to weak localization [21] or due to the confinement of electrons the Drude model becomes invalid.

## 3. Experiment

Our experiments are performed in a combination of a vacuum FTIR spectrometer (Bruker IFS 66 v/S) and a UHV chamber ($<2 \times 10^{-10}$ mbar). This set-up allows in situ measurements during thin film growth under UHV conditions. The metal vapor flux from an electron-beam evaporator (Omicron EFM3) hits the MgO(001) surface at an angle of 37.5° with respect to its normal. The film thicknesses are calculated from the deposition rate (0.15 nm/min) which is calibrated with a quartz microbalance. Ultraclean MgO(001) is prepared in UHV by cleavage of $7 \times 7 \times 15$ $\mathrm{mm}^3$ sized single crystals. Samples, which have been cleaved in air were transferred to high vacuum within 1 h and were baked for 20 h at approximately 200°C. After transfer to UHV these samples were degassed at 450°C for 2 h. The surface structures of both these substrates appear crystalline as judged from LEED. A totally different view is given by our earlier helium-atom scattering measurements, which are sensitive only to the structure of the first layer of atoms. The air-cleaved samples do not show the strong diffraction peaks as found on UHV-cleaved surfaces [4]. Evidently, a large amount of defects remains from exposure to air.

For this study, IR-transmission spectroscopy at normal incidence, from 1400 to 4900 $\mathrm{cm}^{-1}$ with a resolution of 32 $\mathrm{cm}^{-1}$, was performed during Fe deposition at 310 K. The film thickness increases by 0.02 nm while 100 scans are sampled to give one spectrum. For both types of substrate surfaces Fig. 1shows a selection of measured spectra (upper part) and the development of IR-transmission with film thickness (lower part). Broad-band shifts for subsequent spectra and differences in the transmittance for

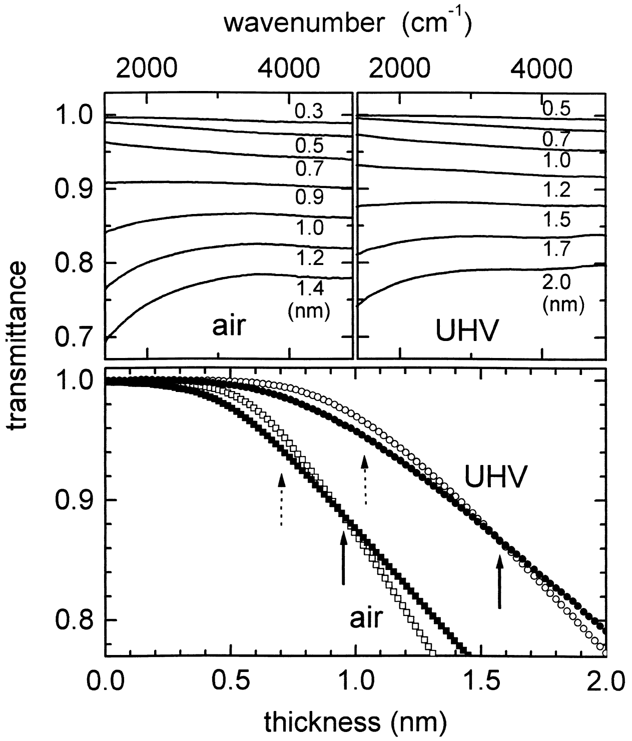

Fig. 1. Upper part: Selection of IR-transmittance spectra from series measured at normal incidence during Fe-film growth. The MgO(100) substrates are at room temperature. Their surfaces are prepared by cleavage in air (left) and by cleavage in UHV (right). Unity means the same transmittance as the substrate. The labels indicate the film thicknesses for the selected spectra. Lower part: Development of IR-transmission at 2000 cm$^{-1}$ (open symbols) and at 4000 cm$^{-1}$ (filled symbols) during Fe-film growth. The MgO(001) substrates are cleaved in air (squares) or cleaved in UHV (circles). The thicknesses of the optical crossover (solid arrows) and upper limits for the d.c.-percolation threshold (dashed arrows, see Section 5) are indicated.

the two surfaces are well resolved. The negative slopes for the transmittance spectra of the thinnest films change to positive slopes at $\sim$1.5 nm for UHV-cleaved surfaces, but already at $\sim$1.0 nm for air-cleaved surfaces. The spectra with almost no frequency dependence indicate this IR-optical crossover [22]. At same thickness, the IR-transmittance for films on air-cleaved samples (FAC) is clearly lower compared with films on UHV-cleaved samples (FUC).

## 4. Calculation of IR spectra

For an interpretation of our IR-optical data we calculate the IR-transmittance spectra of a layer-on-substrate system. We take into account coherent multiple reflections and we use the two-parameter thin-film dielectric function as introduced above. The IR-transmission of the bare MgO substrate is described on the basis of the well-known bulk parameters. The numerical calculations are performed with commercial software [23].

The calculated spectra in Fig. 2 are examples for best-fit results for FAC. They represent the high spectral accordance of measurement and calculation that could be gained for all films above a certain thickness. This accordance (i.e. the minimum of the mean-square error between measured and calculated spectrum, see inset of Fig. 2) gives the values for the thin-film optical parameters $\alpha(d)$ and $\beta(d)$ which are shown in Fig. 2. For demonstrating their importance we calculated the spectrum for, e.g. a 1.5 nm thick film with pure bulk properties ($\alpha = 0$, $\beta = 1$) and we find that in the whole spectral range this IR-transmittance is more than 8% below the values measured for a FUC of same thickness. Even worse results are obtained by ignoring the frequency dependence of $\omega_p(\omega)$ and $\omega_\tau(\omega)$.

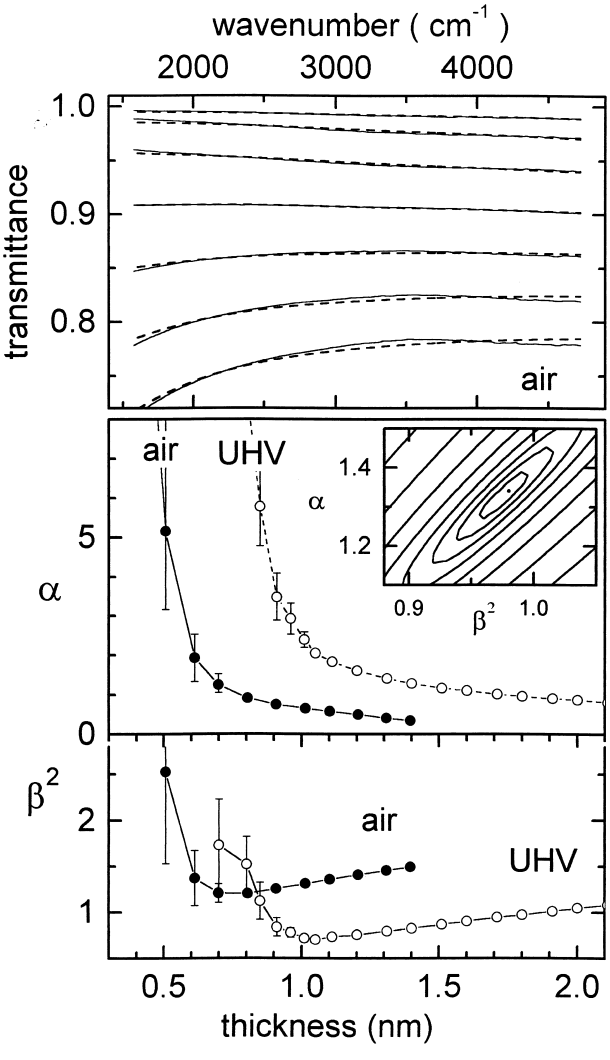

Fig. 2. Upper part: Measured spectra (solid) as shown in Fig. 1 for air-cleaved substrates and best-fit thin film calculation (dashed). Lower part: Fit results for the parameters $\alpha$ (see Eq. (2)) and $\beta^2$ (see Eq. (3)) versus film thickness $d$ for a representative selection of our spectral data for air-cleaved and UHV-cleaved substrates. The inset shows the mean-square error between calculated spectrum and measurement for $d = 1.5$ nm (on UHV-cleaved MgO). Each line indicates an increase by a factor of two. An increase of this mean-square error by a factor of two is used to read out the error bars for $\alpha$ and $\beta^2$.

As a result, the growth of ultrathin Fe ($d \leq 2$ nm) on the different surfaces yields different optical parameters for the two differently prepared films at each thickness. For the onset of the continuous transport properties we consider the well-resolved minimum of $\beta(d)$ at 1.0 nm (FUC) and at 0.7 nm (FAC), respectively. The increase of $\beta(d)$ for smaller thickness has no physical origin. It indicates the breakdown of our model. At even smaller thicknesses, $\alpha(d)$ shows a fast increase which appears like a divergence at a thickness just below 0.7 nm (FUC) and 0.4 nm (FAC). On approaching these thicknesses, the mean-square error of $\alpha(d)$ and $\beta(d)$ rapidly increases. For films thinner than the thickness of the $\beta(d)$ minimum, no well-defined reasonable values for the two fit parameters could be found (see rapidly increasing error bars in Fig. 2).

## 5. Discussion

The measured spectra clearly indicate the large difference in the IR-optical dynamic conductivity of the two types of grown films. For FAC IR-absorption is stronger and metallic-like IR-optical behavior (see optical crossover at 1.6 nm for FUC and at 0.9 nm for FAC in Fig. 1, e.g.) is already revealed at smaller thickness compared with FUC. These differences must be caused by different electronic properties due to a different morphology. Our calculations help to interpret the different optical behavior and to point out its origin.

For a certain thickness, the calculated roughness parameters $\alpha$ indicate an increased electronic relaxation for FUC compared with FAC. As the growth temperature is identical and as the difference in $\alpha$ reduces with increasing thickness, the observed electronic relaxation can not be solely due to atomic (short range) roughness at the surface. Obviously, a granular morphology as a result of a preceding Vollmer–Weber type growth mode [4] additionally shortens the mean free path of electrons and such a morphology is more pronounced on FUC. The fast decrease of $\alpha$ with increasing thickness points at an equalization of that granular structure. This equalization should be the fastest just after having reached homoepitaxial conditions, i.e. having achieved a complete coverage of the substrate surface.

An increasing filling of the effective volume claimed by a granular film is also indicated by the increase of the depolarization parameter $\beta(d)$ above 1.0 nm for FUC and above 0.7 nm for nm for FAC. An increasing volume filling should appear as an increase in $\beta(d)$ as calculated by Bertier and Driss–Khodja [20]. Due to the frequency dependent mean free path the dc-percolation threshold is not detectable in our ac experiments. Nevertheless, the dc-percolation thresholds should be only little below the thickness ranges where the experimental spectra could be well described with our continuous thin film model calculations (i.e. below 0.7 and 1.0 nm for FAC and FUC, respectively).

## 6. Conclusion

Our experiments prove that small differences in the morphology of ultrathin ($\leqslant 2$ nm) films are well detectable with IR-transmission spectroscopy. Combined with a proper dielectric model, information on the morphology and the electronic structure of the films is accessible from the structureless spectra. Careful analysis by inclusion of real bulk properties is essential. Such analysis shows that, e.g. the percolation transition occurs before the optical crossover is observed. We find a granular surface morphology for continuous films of Fe/MgO(001). The dc-percolation transition should occur at a thickness smaller than 1.0 nm on UHV-cleaved surfaces and smaller than 0.7 nm on air-cleaved surfaces.

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