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In-situ investigation of Fe ultrathin film growth by infrared transmission spectroscopy

G. Fahsold *, A. Bartel, O. Krauth, A. Lehmann [1]

Institut für Angewandte Physik, Ruprecht-Karls-Universität Heidelberg, Albert-Ueberle-Str. 3–5, D-69120 Heidelberg, Germany

Abstract

IR-transmission spectroscopy is sensitive to charge transport and charge localization. Applied to low-dimensional metallic systems, this offers the possibility to investigate morphology on a nanometer scale during thin film growth by IR-optical methods. We performed in-situ IR-transmission spectroscopy during deposition of Fe on UHV-cleaved MgO(001) at 313 K and at 121 K. At thicknesses corresponding to a few monolayers of Fe, we find extremely weak IR-absorption that is due to island morphology as known from our previous helium-atom-scattering results for the same system. For complete substrate coverages, the comparison of IR-transmittance with calculations for homogeneous films indicates significant attenuation of IR-absorption due to additional scattering of charge carriers at the irregular surface as a result of preceding island growth. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Infrared spectroscopy; Iron; Thin films

1. Introduction

Dielectric properties of thin films strongly depend on morphology. As metals tend to form islands on insulating substrates [1], these films appear at a low film thickness as two-dimensional homogenous insulators. Effective medium theories (EMT) have been established to describe their optical properties [2]. With increasing thickness, these films approach a cross-over in conductivity, called percolation. A large amount of effort has been made to investigate the optical properties accompanying this transition [3]. The optical cross-over of fractally structured semicontinuous Ag films has been described on the basis of fractal renormalization [4]. All these approaches almost ignored the specific intrinsic electronic structure of low-dimensional systems. Classical size effects (CSE) [5], known from, for example, the damping of optical resonances of small metallic particles, and quantum size effects (QSE) [6], observed, for example, in electron spectroscopy from ultrathin metal films [7], have to be considered. Weak localization, as observed by thin-film d.c.-conductivity measurements [8], might also contribute to optical properties. An experiment with thin films that rapidly cover the substrate might shine some light on the relation between IR transmittance, film morphology, and electronic structure.

In this paper, we report on a comprehensive study of IR transmittance, HAS (helium-atom scattering) specular reflectivity, and IR-optical model calculations for ultrathin Fe/MgO(001). From our detailed HAS study of epitaxial Fe/MgO(001) [9], we know that at room temperature and below, the substrate is already completely covered at a sub-nanometer thickness.

* Corresponding author. Fax: +49-6221-549262.
E-mail address: fahsold@urz.uni-heidelberg.de (G. Fahsold)
[1] New surname: Pucci.

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When comparing IR transmittance and HAS results, we will refer to the following findings: HAS specular reflectivity of Fe grown at room temperature and below is more than two orders of magnitude smaller than the reflectivity of MgO(001). The reflectivity for an incomplete Fe coverage is therefore mainly due to substrate scattering, whereas for a complete coverage, it is a measure of surface smoothness [10].

For IR-spectral calculations, we take into account coherent multiple reflections (SCOUT-94 software package for optical spectroscopy; Soft Science, Aachen, Germany), and we use a continuous-thin-film model dielectric function that is based on Drude's formula but considers real Fe-bulk dielectric properties [11] by frequency-dependent relaxation and charge carrier density, respectively. CSE due to electron-surface scattering are included in the typical relaxation-time approximation [5]. As the thickness of the investigated films is smaller than the electron mean free path (~ 100 Å at $2000\ cm^{-1}$), we treat all charge carriers in the same way. We also allow a small thickness-dependent reduction of bulk plasma frequency to account for QSE [6] and surface effects with respect to electronic polarization. The theoretical treatment for inhomogeneous island films will be discussed in a forthcoming paper [12].

2. Experiment and results

We performed IR-transmission spectroscopy with a vacuum FT-IR spectrometer (Bruker IFS 66 v/S) and a liquid-nitrogen cooled MCT detector, both connected to a UHV ($<2\times10^{-10}$ mbar) chamber via KBr windows. A water-cooled evaporator enables Fe ultrathin film preparation. The deposition rate, typically $3\ Å\ min^{-1}$ (assuming Fe-bulk density), is calibrated for each experiment with a quartz microbalance. Ultraclean MgO (001), with dimensions of $7\times7\ mm^2$, was prepared by crystal cleavage in UHV.

During thin-film deposition at various substrate temperatures, IR-transmission spectroscopy was performed at a sampling rate of one spectrum (100 scans) during an approximately 0.4 Å increase in film thickness. These spectra ($1200–6200\ cm^{-1}$) were taken with a resolution of $32\ cm^{-1}$ at normal incidence. As a reference, the MgO transmission is measured prior to film preparation.

The results of our IR-transmission spectroscopy are shown in Figs. 1 and 2 for two different

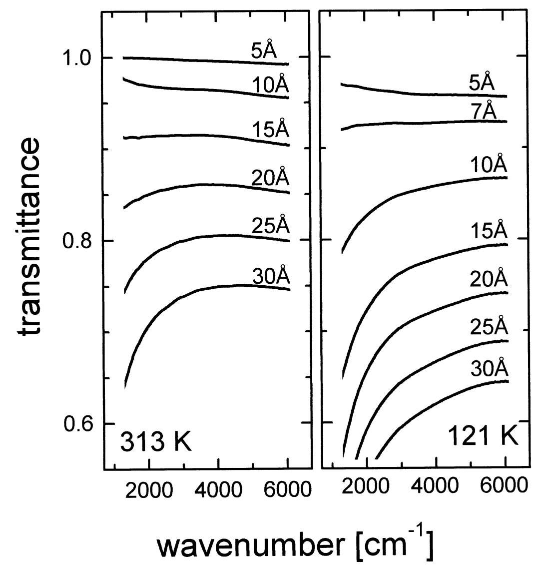

Fig. 1. Transmittance spectra (normal incidence) of Fe growing on MgO(001) at various temperatures (313 and 121 K). Unity means the same transmittance as the substrate. The labels indicate the film thickness (see text).

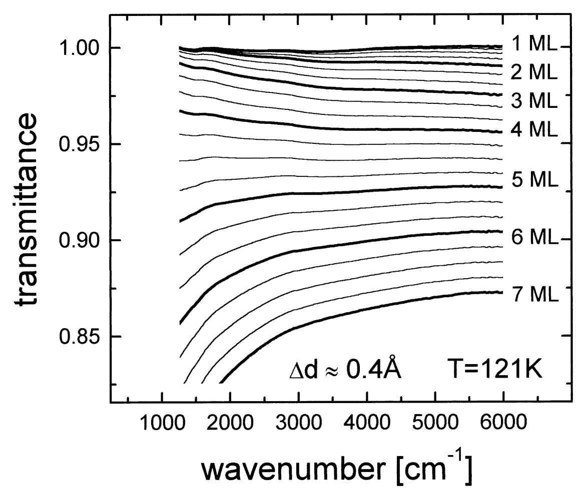

Fig. 2. As Fig. 1, but for very low thicknesses at 121 K. From spectrum to spectrum, the thickness increases by ~ 0.4 Å. Bold lines indicate approximately complete Fe monolayers (ML).

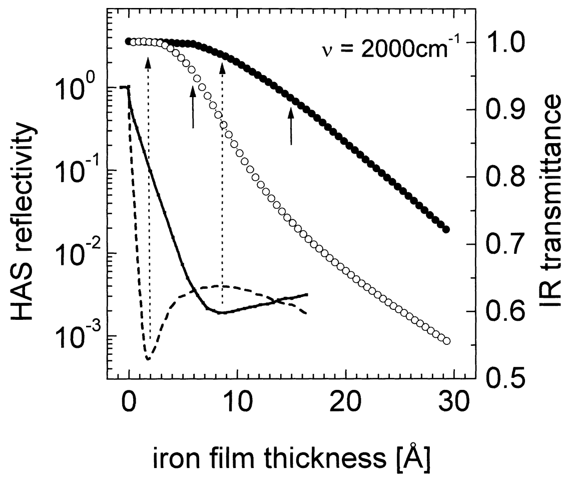

Fig. 3. Change in Fe thin film transmittance (at 2000 cm^{-1}) with increasing film thickness. The substrate temperature is 121 K (open circles) and 313 K (solid circles). The lines in the lower part of the figure show the HAS reflectivity for the growth of the same system at similar temperatures, i.e. at 140 K (dashed line) and at 300 K (full line). The minimum of HAS reflectivity (dotted arrows) and the optical cross-over (full arrows) are indicated.

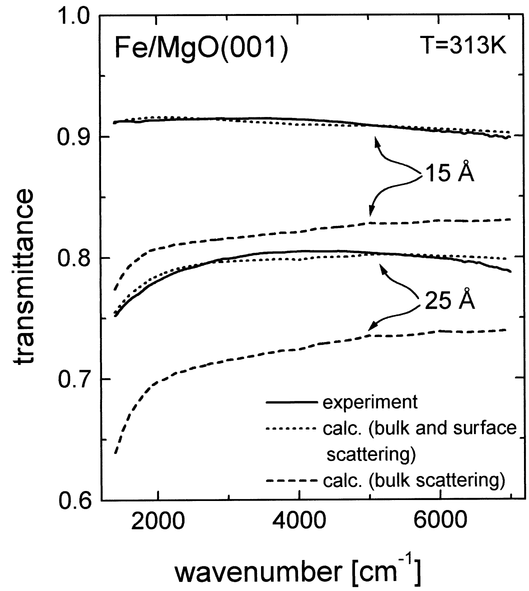

Fig. 4. Transmittance spectra (as in Fig. 1) for Fe thin films of 15 and 25 Å thickness, respectively, on MgO(001). Full line: experimental result for growth at 313 K. Dotted line: best fit result assuming real bulk dielectric properties and additional electron-surface scattering (see text). Dashed line: calculation result assuming real bulk dielectric properties but no size effects. Obviously, calculations omitting size effects fail in describing the experimental curves.

substrate temperatures (121 and 313 K) and for the various film thicknesses as indicated. The series of consecutively measured spectra (Fig. 2) demonstrates that broad-band shifts in IR transmittance are well resolved down to a sub-ångström increase in thickness. We observe negative slopes for the spectra of the thinnest films but a cross-over to positive slopes around 6 Å at 121 K and around 15 Å at 313 K. The transmittance decreases in the whole spectral range with increasing film thickness, the stronger the lower the temperature. Only at the very beginning of metal deposition does the transmittance not decrease remarkably (see Fig. 3).

These results will be discussed in comparison with our HAS-reflectivity data (see Fig. 3) for growth temperatures close to those used above. They show a rapid decrease in reflectivity for a small film thickness and a minimum at 1.8 Å (140 K) and at 8 Å (300 K), respectively, followed by a weaker increase.

Finally, the theoretical spectra in Fig. 4 (dotted) are the best fit results for films at room temperature. The single fit parameters are a scaling factor for the bulk-plasma frequency and a surface-scattering rate, which is added to the bulk-scattering rate. For films with thicknesses of 15 and 25 Å, the best-fit values are 0.82 and 0.91 for the reduction of bulk plasma frequency and 8.6×10^{-14} and $4.6\times10^{-14}\,s^{-1}$ for the surface-relaxation rate, respectively. Generally, by applying the continuous-film model mentioned above to the 313 K films, we find a good spectral agreement for films thicker than 8 Å with reasonable values for the only two fit parameters [12].

3. Discussion

Our IR results clearly demonstrate that morphology depends sensitively on growth temperature. Nevertheless, it appears uncertain how to correlate spectral features like the change in dispersion and the thickness dependence of transmittance level to distinct phases of thin-film growth, e.g.

percolation. To enlighten this problem, we first discuss our results in comparison with HAS-reflectivity data. Our dynamic-conductivity calculations will further illuminate the influence of electronic structure on the observed spectral behavior.

Growth on MgO(001) at low temperature leads to iron films that cover the substrate surface more rapidly than at room temperature. We can make this conclusion from the temperature-dependent onset of metal-like (strong) IR absorption. We define the film thickness of this onset (~4 Å at 121 K and ~8 Å at 313 K) as the point of maximum curvature of the transmittance curves in Fig. 3. Around room temperature, this thickness coincides well with the minimum of HAS reflectivity. This minimum indicates the completion of substrate coverage. The weak IR absorption at smaller thickness is due to the dielectric response of a more or less interconnected island structure. For growth below room temperature, the HAS reflectivity minimum is found at a smaller thickness (~2 Å) than the onset of IR absorption, which certainly indicates that complete metal coverages show almost no absorption at a very low thickness. This observation clearly differs from an almost linear decay of transmittance as estimated for homogenous films with bulk properties [13]. Weak localization [8] and enhanced electron scattering due to grain boundaries and surfaces are probably the origin. At a higher growth temperature, grain boundaries are washed out during growth, and even before complete coverage is achieved, clusters much larger than the electron mean free path are formed.

Nevertheless, complete coverages with the same thickness (>10 Å) show a stronger absorption for a low growth temperature and a weaker absorption for growth at room temperature. This should be due only marginally to the temperature dependence of phonon scattering but mainly due to the higher filling factor of the low-temperature film. In another paper, we will present this finding in more detail [12].

We now turn to the spectral properties of the prepared films. In the frequency range investigated, an optical cross-over [4], i.e. almost constant transmittance, is observed around a thickness of 6 Å at 121 K and of 15 Å at 313 K. In the range of smaller thickness, the decrease in transmittance with frequency is reminiscent of IR absorption from metallic particles in non-metallic matrices [14]. In these systems, the monotonic increase of IR-optical constants with frequency is due to the approach towards electromagnetic resonances. However, in our case, a negative slope of spectral transmittance is observed even for films that already completely cover the substrate, i.e. between 2 and 6 Å at 121 K and between 8 and 15 Å at 313 K. From our model calculations accounting for real dielectric bulk-properties and including CSE (see Fig. 4), we conclude that frequency- and thickness-dependent electronic scattering is responsible for the observed extraordinary spectral behavior. It follows that the optical cross-over in ultrathin metallic films is driven by the real electronic structure, which is of fundamental importance for the investigation of morphology by means of IR-optical methods. For Ag/KBr, which shows pronounced island growth, the optical cross-over was attributed to percolation [4]. From our experiment, we find for the rapidly covering Fe/MgO(001) that percolation occurs far before the optical cross-over. Therefore, we propose to analyze the surface scattering rate (as best-fit results for calculated spectra) to investigate the morphology of these ultrathin metallic films. Up to now, we find that the scattering rate diverges at about 8 Å thickness at 313 K. Obviously, morphology basically changes around 8 Å, which is in good agreement with our findings from HAS reflectivity.

For a higher thickness (>40 Å), our electronically homogeneous-film model calculations fail to describe the experimental results for Fe/MgO or Fe/KBr [13]. This is due to the finite mean free path of electrons, e.g. 100 Å at 2000 cm^{-1}. With increasing thickness, near-surface regions of the film should be treated in a different manner to the inner part.

4. Summary

Our infrared-transmission experiments show that information on ultrathin film morphology is accessible via IR-optical methods; however, due to the thickness-dependent electronic structure, careful analysis of IR-data is essential. For example, the onset of strong IR-absorption correlates with the completion of substrate coverage. We found an optical cross-over (i.e. almost frequency-independent IR transmittance) that is driven by electronic structure and electronic scattering but not by a percolation transition.

Our experiments demonstrate the power of an IR-spectroscopic investigation of electronic structure during thin-film growth. More detailed information from the spectra demands a further development of theory for ultrathin inhomogeneous films.

Acknowledgements

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