I. INTRODUCTION

Cr is a bcc metal under normal conditions, but grown as thin films, it may show different phases.1–3 For example, for Cr layers with \( d = 2.5 \) nm on Au, an fcc structure was suggested from x-ray diffraction measurements.1 Theoretically it was predicted, that for Cr nanoclusters with diameters \( d < d_{\text{crit}} = 2.5 \) nm the total energy for the fcc phase is lower then for the bcc phase due to the lower surface energy.4 In Ref. 5 the fcc structure of Cr nanoclusters below the critical size of \( \sim 2.5 \) nm was proven by x-ray diffraction from cluster aggregates and by transmission electron microscopy. Because of its good adhesion, Cr is frequently used as interlayer for metallization. For example, the system Cr on diamond shows different phases.5,6 Despite the manifold application of ultra high vacuum conditions reveal a structural phase transition from a discontinuous phase to the crystalline bulk one with Drude-type optical properties. The thickness of 2.5 nm of the observed phase transition well agrees with literature data on the theoretically predicted maximum size for stable fcc nanoclusters the formation of which should be supported on C(100) owing to a good lattice match. Below 2.5 nm, the spectral behavior surprisingly well corresponds to a Drude-Smith type dielectric function, which allows one to determine the conductivity for the discontinuous phase and to get quantitative information on the effect of coherent backscattering.

II. IR PROPERTIES OF CR AND CONDUCTIVITY MODELS

The IR properties of bcc Cr can be reasonably described by the Drude model for the (relative) dielectric function,

\[
e(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\tau},
\]

with the background permittivity \( \varepsilon_{\infty} \), usually set to unity in the IR, and the two Drude parameters plasma frequency \( \omega_p \) and relaxation rate \( \omega_r = 1/\tau (\epsilon_0 \text{ is the permittivity of vacuum}) \). The corresponding complex optical conductivity \( \sigma(\omega) \) is related to \( e(\omega) \) by

\[
\sigma(\omega) = -i[\varepsilon_{\infty} - \varepsilon_0] \epsilon_0 \omega.
\]

As it follows from optical data for bulk Cr in Ref. 18, interband contributions can be neglected up to \( \omega_{\text{max}} \approx 1500 \text{ cm}^{-1} \), i.e., up to this wave number the reported data well correspond to the Drude model with the parameters 36 650 cm\(^{-1}\) and 440 cm\(^{-1}\) for \( \omega_\text{p} \) and \( \omega_\tau \), respectively.

Continuous ultrathin metal films in the mid IR can be well described with the Drude model, if \( \omega_r \) and \( \omega_\tau \) are considered
as thickness-dependent parameters. A thickness dependence of ωp is related to the scattering of conduction electrons at surfaces [classical size effect (CSE)]. The CSE leads to a roughness-dependent surface contribution ωp,0(d) that is proportional to the inverse film thickness 1/d. Additionally, crystalline defects in the film may differ from sample to sample. Scattering at defects might be more pronounced in as grown ultrathin films and, according to Matthiessen’s rule, might furthermore increase the relaxation rate by ωp,1. Hence, the thickness-dependent total relaxation rate is

\[ \omega_p(d) = \omega_p^{\text{bulk}} + \omega_p,0(d) + \omega_p,1(d). \] (3)

The change in ωp with thickness in thin films arises from quantum size effects, contributions from surface states, and depolarization effects. The Drude model (in the refined version by Sommefeld) is based on the relaxation time approximation. The collisions are assumed as infinitely short, as independent from each other, and as completely effective in obliterating any information about the electron configuration before the collisions. The last assumption means the complete loss of phase coherence and the destruction of the wave function before the collisions. The last assumption means the approximation. The collisions are assumed as infinitely short, leading to a roughness-dependent surface contribution IR27 and terahertz regime.28–30 The Drude-Smith model basically assumes that phase coherence is completely lost after a series of collisions. Supposing persistence of velocity after the first collision (single-scattering approximation) the complex dielectric function of the Drude-Smith model reduces to

\[ \varepsilon(\omega) = \varepsilon_0 - \frac{\omega_p^2}{\omega^2 + i\omega\tau}, \]

Here, in classical terms, the coefficient c represents that fraction of the electron’s velocity in forward direction that, on average, is retained after a collision. This is the so-called memory or persistence of velocity effect. For elastic collisions, the parameter c corresponds to the expectation value of \( \cos(\theta) \) where \( \theta \) is the scattering angle. Accordingly, c=0 means isotropic scattering which gives a Drude-type metal and c=1 means full backscattering of electrons, which corresponds to an insulator. Extrapolation to the static limit gives the dc conductivity

\[ \sigma_{dc} = (1 + c)\varepsilon_0\omega_p^2/\omega, \] (5)

III. EXPERIMENTAL

The experiments were performed in an UHV chamber with a base pressure of 1 · 10^{-10} mbar and 2 · 10^{-10} mbar during Cr deposition. The substrate was a commercial CVD diamond C(100) single crystal, supplied by Element 6, with dimensions 5 × 5 × 0.5 mm^3. Prior to transfer into UHV it was cleaned in a boiling 1:1:1 solution of HNO₃:H₂SO₄:HClO₄. This treatment was carried out to remove amorphous carbon, additionally leading to an oxygen terminated p(1×1) surface. Once transferred into UHV, the diamond was heated to 350 °C for several hours. Afterward, a LEED pattern was observed indicating a well prepared C(1 0 0)1 × 1 surface. Cr was deposited by an electron-beam evaporator (Micon) at a rate of about 1 Å/min from a tungsten crucible. The rate was calibrated with a quartz-micro-balance before and after the experiment, which leaves an error of 10% in thickness and, consequently, of at least 5% in the fit parameter plasma frequency. The average film thickness was calculated from the measured average deposition rate and the time using the bulk density of Cr(7.14 g/cm^3).

During deposition the substrate was kept at room temperature. The IR spectrometer (Bruker IFS 66 v/S) and the HgCdTe (MCT) IR detector were coupled to the UHV chamber via KBr windows, so the spectra were taken during film growth. The spectral resolution was 8 cm⁻¹, data acquisition for one spectrum took about 45 s (corresponding to a thickness change of less than 1 Å during one spectrum). All spectra are relative transmittance measurements at normal incidence (electric field parallel to the layer) with the bare diamond as reference.

Ex situ atomic force microscopy (AFM) measurements were performed immediately after exposure to air with a Multimode scanning probe microscope (Veeco SPM) in contact mode.

IV. RESULTS AND DISCUSSION

Figure 1(a) shows the development of the relative transmittance during Cr deposition for various selected frequencies. According to the spectral development with thickness, three different phases (I, II, III) can be distinguished [see Fig. 1(a)]: In phase I, up to ~0.5 nm, no change in transmittance is observed. Such behavior is typical for the formation of a non-conductive wetting layer. In phase II, up to ~2.5 nm, the transmittance is almost frequency independent, but decreases linearly with increasing d. For such ultrathin films (optical thickness ≪ wavelength), Fresnel’s equations give a transmittance change that is linearly proportional to thickness and to the real part of the dynamic conductivity. Thus, from that linear change it follows that the IR dynamic conductivity of phase II seems not to change with thickness, which is clearly different to metal films with qualitative changes in their morphology during growth. Moreover, the frequency-independent spectrum of phase II is typical for metal-particle systems at percolation. In metal-island films before percolation, the formation of separated metal islands usually is indicated by a transmittance with negative slope vs frequency, which is explained as the red tail of particle plasmon resonances.7,32 The interaction between particles produces a red shift of the low-frequency tail of the optical absorption.

For film growth via metal-island formation, percolation occurs at a certain average thickness and is not extended to a thickness range of several monolayers. The denser the nucleation centers for island formation the lower the average
thickness for percolation, which in case of metal-island formation gives a percolation threshold that significantly depends on temperature. From percolation on, coalescence and lateral growth of the crystalline area proceed, which results in a clear metallic dispersion in IR transmittance. Comparison of those features of island-like films to the Cr growth observations leads to the only conclusions that Cr film percolation is reached already at the very low-average film thickness of about 0.7 nm and that during further Cr deposition, the nanoislands do not coalesce to bigger grains and do not form a crystalline layer for some reason. Instead, up to the average thickness of ~2.5 nm, the individual islands can grow in their height only. Then, in phase III, for \( d > 2.5 \) nm, the transmittance increases with increasing wave number, as expected for a Drude-type metal layer.

We will now proceed with a detailed discussion of the dynamic conductivities in phase III and II, and of the transition from II to III. We start with the thickest films since they show well-known Drude-like behavior.

### A. Films with Drude-like conductivity

A selection of recorded spectra and respective Drude-fit curves for the range of 500 cm\(^{-1}\)–1500 cm\(^{-1}\), based on the dielectric-function from Eq. (1) with \( \omega_p \) and \( \omega_\tau \) as fit parameters are shown in Fig. 1(b). The fits were performed with the software package SCOUT,\(^{34}\) which exactly considers the thin film optics. Very good accordance for films beyond 2.5 nm is obvious, see Fig. 1(b).

Figure 2(a) displays the obtained Drude parameters. For films with \( d < 2.5 \) nm, the fit provides unreasonable parameters. The relaxation rate corresponds to a mean free path for the electrons of less than one atomic distance, contradicting the Ioffe-Regel criterion\(^{35}\) and indicating a breakdown of the free-electron model.

For \( d > 2.5 \) nm, the Drude-type fit provides reasonable values for the two parameters. \( \omega_p \) reaches a constant value at...
higher $d$. The deviation of only 6% to the bulk value may be related to the error of the thickness calibration. $\omega_z$ becomes linearly dependent on $1/d$ at higher $d$, as shown in Fig. 2(b). This is expected from the CSE for constant film roughness and structure [see Eq. (3)]. An extrapolation of $\omega_z$ for $1/d$ toward 0 ends up at a more than two times larger value compared to $\omega_{\text{bulk}}$, indicating a defect rich polycrystalline film with lower dc conductivity than that following from published data of bulk Cr. However, by increasing the substrate temperature to $T=400$ K, the crystalline quality of the Cr films can be significantly improved, which in our IR studies gives spectra that correspond to lower relaxation rates.36

B. At the phase transition

At $d=d_{\text{crit}}=2.5$ nm both the Drude parameters approach rather high values, see Fig. 2(a). Furthermore, the derivative of the transmittance with respect to $d$ exhibits an extremum at $d=2.5$ nm, as shown in Fig. 3. Both these arguments indicate the strong change in the morphology of the film at $d_{\text{crit}}$. It has to be mentioned that the origin of the sudden spectral change at $\sim 2.5$ nm is unlikely a transition from the antiferromagnetic to the paramagnetic state as the Néel-temperature is expected to be well below room temperature for such thin Cr films.37 Measurements at various different substrate temperatures36 gave the surprising result that the IR spectra below $d_{\text{crit}}$ and $d_{\text{crit}}$ itself only negligibly depend on temperature, clearly different to the case of island-like growth where the critical thickness for the transition to a conducting layer is observed to decrease with decreasing temperature and strong spectral changes are observed.7 The nearly temperature independent $d_{\text{crit}}$ also contradicts amorphous growth effects due to hampered diffusion at low temperatures.38 Accordingly, another reason that is not related to diffusion properties, should exist for the transition from the discontinuous phase to the bcc polycrystalline one. Since good arguments were already given on the energetically favored formation of fcc nanoclusters up to diameters of $d<2.5$ nm, the transition from that phase to the bcc bulk one certainly can be considered as the main reason for the sudden change observed in IR spectra at 2.5 nm. Additional support for this interpretation of a dominant fcc Cr phase in the initial stage of the growth is given by the better lattice match for diamond and fcc Cr. While the mismatch is 14.3% for bcc Cr ($a_{\text{bcc}}=2.52$ Å, $a_{\text{Cr}}=2.88$ Å), it is only 1.4% for fcc Cr ($a_{\text{Cr}}=3.57$ Å, $a_{\text{Cr}}=3.62$ Å (Ref. 39)). Our AFM data presented in Fig. 4 corroborate our interpretation of the phase transition. While for $d<d_{\text{crit}}$ the AFM image shows small, uniform nanoparticles, for $d>d_{\text{crit}}$ expanded homogeneous structures are observed. Unfortunately, the precise value for the nanoparticle size cannot be directly taken from the image, since it represents a convolution of the tip contour and the nanoparticle geometry. However, the obvious nanoparticle size in the image can be considered as the upper limit of the real size and, thus, is in agreement to the prediction for critical cluster size.

C. Conductivity of the discontinuous phase

According to the above mentioned arguments phase II certainly consist of densely packed nanocrystals and is therefore not amorphous. Accordingly, the conductivity should not be fully suppressed due to charge carrier localization. Indeed, the extremely weak frequency dependence of IR transmittance in phase II rather points to a nonvanishing static conductivity40 than to an insulating behavior. Because of these two reasons we tried to get useful conductivity parameters from spectral fits to the Drude-Smith model which, in contrast to the Drude model, accounts for coherent back-
scattering effects as they may occur in a dense package of nanocrystallites.

Fit results from the Drude-Smith model for spectra of films with $d < d_{\text{crit}}$ are shown in Fig. 5. Excellent accordance between calculations (based on Eq. (4)) and experimental data is obvious. It has to be noticed that fits with Drude-Smith model beyond the single-scattering approximation do not improve the accordance to experiment. Figure 5 also shows the extrapolation of the fit curves to the dc limit. The dc values with relative transmittance <1 (and thus, with $\sigma_{\text{dc}} > 0$) indicate conductive layers from 0.7 nm on.

Figure 6 summarizes the Drude-Smith parameters for the whole thickness range. The persistence of velocity parameter $c$ equals −1 for the transition from phase I to phase II before steeply rising to $\sim 0.5$ in phase II. There, from about 1 nm on, the parameter stays nearly unchanged for a range of 1.5 nm before rising abruptly to a value close to zero. Au on Si produced by cluster deposition was reported to show similar behavior in $c$. The results can be interpreted in the following way: when $c = -1$ the dc conductivity of a film is completely suppressed, while for $-1 < c < 0$ the dc conductivity is nonzero. The specially interesting finding is the constant value for $c$ of around −0.5 over a rather broad thickness range. It indicates backscattering of the same amount while the average film thickness is increasing. An explanation could be this: Densely packed fcc Cr nanoislands grow in height under conservation of the lateral structure and, therefore, the measured in-plane conductivity is marginally effected. As it could be seen from the values given in Fig. 6, the parameters $\omega_p$ and $\omega_\tau$ of the Drude-Smith-type fit correspond to reasonable values throughout the whole film growth. In phase II, the increasing value of $\omega_p$ is not related to the Drude-Smith model. Instead it could be a hint that quantum size effects strongly alter the carrier density, as it is expected for films in that thickness range, where $d$ is comparable to the wavelength of the electrons. The overshoot of $\omega_p$ above $\omega_p^{\text{bulk}}$ for 2 nm $< d < 2.5$ nm corresponds to a higher plasma frequency for fcc Cr compared to bcc Cr, an assumption supported by calculations in Ref. 41. For $d < d_{\text{crit}}$, $\omega_\tau$ changes only slightly. At $d_{\text{crit}}$, $\omega_\tau$ exhibits a discontinuity as expected at an electronic percolation transition. Since $c$ is very close to 0 for $d > 2.5$ nm, the results from the Drude-like fit are reproduced for $\omega_p$ and $\omega_\tau$ in this thickness range. So, for phase II, the successful Drude-Smith-type fits to a series of spectra demonstrate that it is possible to describe experimental IR spectra of an unusual phase with reasonable parameters.

V. SUMMARY

In summary, with sensitive IR spectroscopy during film growth a structural phase transition in ultrathin chromium was observed at a film thickness of 2.5 nm. At higher thickness, the Cr films show the Drude-type behavior with a relaxation rate that is modified according to the classical size
effect. The critical thickness itself and the IR spectral properties of the Cr films at lower thickness corroborate the old theoretical finding of preferred fcc nanocluster formation. The sequence of IR spectra of that phase can be well described with the Drude-Smith model. The respective fit parameters represent reasonable values, as explained, and, moreover, the special parameter c indicates partially coherent backscattering of electrons, which may be seen as indicative of the nanocrystalline array.

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