Resistance oscillations and crossover in ultrathin gold films

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The resistivity of thin single-crystalline Au and Ag layers is measured during deposition onto Si(111) surfaces at 95 K from zero to several tens of monolayers and for layers from 1.5 to 12 monolayers as a function of temperature. The structure of the layers is monitored by reflection high-energy electron diffraction (RHEED). In Au layers resistance oscillations occur synchronously with RHEED intensity oscillations. They are attributed to periodic variations of the specularity factor. Below 6 monolayers a three- to two-dimensional crossover is observed.

I. INTRODUCTION

The exciting physical properties of low-dimensional systems which have been predicted theoretically[1] can be particularly well studied in two dimensions (2D) because the theoretical 2D systems can be approximated experimentally in the form of thin deposited films or thin semiconductor inversion layers. Unfortunately, the thin-film approach has been limited up to now to relatively thick films because the films become discontinuous below a critical thickness which depends upon film and substrate material, deposition temperature, rate, and other parameters such as residual gas pressure. Furthermore, most films have a rough surface and a high density of grain boundaries due to their polycrystallinity[2-5] which complicates the analysis of the experimental results in terms of the various theoretical models.

The continuing evolution of the theory of quantum interference phenomena[6-9] calls for experiments on well-defined systems for verification. Such systems are high-purity ultrathin single-crystal metal films with atomically flat surfaces and precisely known thickness. The closest approach to fulfilling these conditions was achieved by Chaudhari *et al.*[10] who prepared Au single-crystal films of less than 10 nm—but not precisely known—thickness by epitaxy on epitaxial Ag films. In this paper we report results for well-characterized continuous Au films which are an order of magnitude thinner and, therefore, should exhibit quantum size effects more clearly.

II. EXPERIMENT

In order to obtain single-crystal films of the order of 1 nm (or less) thickness on (semi-)insulating substrates, surface preparation and vacuum conditions are of utmost importance. Our Au films were, therefore, prepared in an ultrahigh vacuum (UHV) system pumped by an ion pump and a Ti sublimation pump with liquid-nitrogen (LN$_2$) cooled cold wall which achieved a base pressure of

8×10^{-11} mbar and kept the pressure during deposition below 3×10^{-10} mbar. The substrates were well-oriented Si(111) wafers with about 10 Ω cm specific resistance at room temperature and typical dimensions $12 \times 3 \times 0.6$ mm^3. The crystals were mounted with Ta clips on a holder which allowed rotation about the substrate normal so that studies in various azimuths were possible with the reflection high-energy electron diffraction (RHEED) system attached to the vacuum chamber. The initial chemical cleaning was followed by a final cleaning after bakeout consisting of a flash of a few seconds by direct resistive heating to about 1550 K which produced a good (7×7) RHEED pattern. This pattern was further improved by predeposition of about one monolayer (ML) Au followed by a 3 min anneal at about 1050 K and flashing off the Au at 1550 K. The specimen could be cooled to 100 K by making thermal contact to a LN$_2$ container. Au was evaporated from a W basket shielded by a LN$_2$-cooled cold wall with typical rates of about 0.05 nm/s which was measured with a quartz-crystal monitor.

The structure of the substrate and the growing Au layer were monitored by RHEED with a 20-keV electron beam. A photodiode with a 0.5-nm-diam aperture was used to record the intensity of the specular beam. The polar angle could be adjusted to about $\pm 0.1°$, the azimuthal angle to $\pm 1°$ with respect to the Si RHEED pattern. All intensity measurements were made at angles far below the first Bragg maximum in order to enhance the surface sensitivity.

The resistivity and the RHEED specular beam intensity were measured on the same substrate as follows. The 1017-Hz signal from an ac generator was multiplied with the dc signal from the quartz-crystal monitor which is proportional to the mass of the deposited film. The monitor was calibrated by x-ray diffractometry of Pb/Ag epitaxial superlattices which were prepared in the same system.[11] The ac-dc product voltage was applied to the Si substrate—which had a typical resistance of about 1 kΩ at 95 K—with a 330-kΩ resistor in series. This circuit gave a constant current density through

the Au film of about 1 μA/nm independent of film thickness d. A signal which is proportional to $R_{\parallel}d$ with $R_{\parallel}=R_sR_f/(R_s+R_f)$, where R_s is the resistance of the substrate, R_f that of the film, was obtained from potential contacts consisting of electrochemically etched W wires pressed against the Si crystal. In this manner the film resistance could be measured with high accuracy within a broad dynamic range from 10 000 to 10 Ω. The signal was measured with a lock-in amplifier and was both recorded on a X-Y recorder and stored in digital form for further evaluation.

III. RESULTS

A typical result for a RHEED specular beam intensity (I) and resistivity (ρ_f) measurement is shown in Figs. 1(a) and 1(b), respectively. In order to bring out the details of the $\rho_f(d)$ curve, the Sondheimer approximation for $d/l>1$ (l mean free path) to the Fuchs formula[2-4]

$$\rho_0(d)=\rho_\infty\left[1+\tfrac{3}{8}(1-p)\frac{l}{d}\right]$$ (1)

was subtracted and the difference normalized to ρ_0. Here ρ_∞ is the specific resistivity of the bulk material and p is the fraction of electrons which have been scattered elastically at both surfaces of the film. The values for ρ_∞ and $(1-p)l$ chosen in Fig. 1(b) will be discussed below. Here we focus on the oscillations seen in $\rho_f(d)$. A comparison with the $I(d)$ oscillations in Fig. 1(a)—which become exactly equidistant after 3 ML—shows that the $\rho_f(d)$ oscillations are intimately linked with the $I(d)$ oscillations: the minima of ρ_f coincide with the maxima of I.

Thus, an understanding of the ρ_f oscillations requires an understanding of the I oscillations of the specular beam. Such oscillations have originally been observed in GaAs molecular-beam epitaxy (MBE)[12] and recently also in metal MBE on metals[13,14] in which monolayer-by-monolayer growth [Frank–van der Merwe (FM) growth mechanism] may be expected.[15] Their appearance in a metal layer on a semiconductor surface is unexpected and shows that after an initial transient of about 3 ML Au can be grown in the same manner at sufficiently low temperatures. That this phenomenon is not limited to Au can be seen in Fig. 2 which shows corresponding oscillations for a Ag layer. Here, the oscillation period is constant down to the first monolayer which indicates FM growth from the very beginning.

Interestingly, the $\rho_f(d)$ curve for Ag corresponding to Fig. 2 does *not* show oscillations. Furthermore, while ρ_f approaches ρ_0 very rapidly for Au—at about 15 ML— ρ_F for Ag passes through a minimum at about 20–30 ML and rises then slowly again. This unusual behavior of Ag can be understood on the basis of the structural changes occurring in Ag films with increasing thickness as seen in RHEED: Up to the ρ_f minimum Ag is singly positioned, i.e., there is no twinning observable, with very sharp streaks in the RHEED pattern indicating large crystal size. Beyond the minimum double positioning is seen initially and later a ring diagram develops. The increase of ρ_f with d is thus connected with the formation of grain boundaries resulting in grain-boundary scattering and later, in addition, with increasing surface roughness which causes a decrease of p and, consequently, an increase of ρ_f according to Eq. (1).

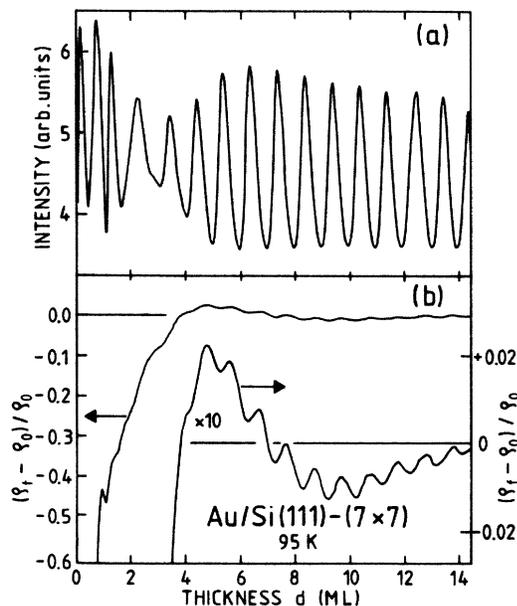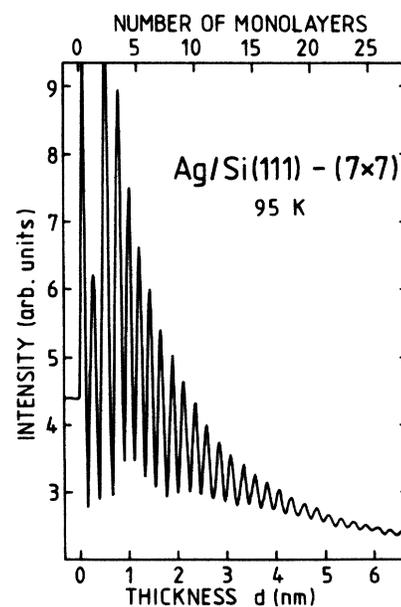The absence of ρ_f oscillations in Ag in contrast to Au shows that monolayer-by-monolayer growth *per se* does

FIG. 1. RHEED specular beam intensity oscillations (a) and resistivity oscillations (b) during growth of a Au film on a Si(111)-(7×7) surface at 95 K. For explanation see text.

FIG. 2. RHEED specular beam intensity oscillations during growth of a Ag film on a Si(111)-(7×7) surface at 95 K.

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not cause ρ_f oscillations. An additional condition must be fulfilled which is again suggested by RHEED. While the Ag RHEED streaks are sharp, those of Au are broad independent of d above 3 ML. Thus, Au forms small crystals with a large number of surface steps whose density varies periodically just as on the growing Ag layer surface on which their density is, however, much smaller. Electron scattering on surface steps is diffuse but specular on the flat surface.[2-4] Therefore, the periodic modulation of p is clearly visible on the high step density Au layer but it is below the detection limit of our measurements on the low step density Ag layer.

It might be argued that the ρ_f oscillations are due to the quantum size effect for the conduction electrons. This would give an oscillation period $d_0 = \lambda_F/2$ (Refs. 2-4) where λ_F is the Fermi wavelength in the $\langle 111 \rangle$ direction, $\lambda_F = 0.353$ nm. This is clearly incompatible with the observed period which agrees with the Au monolayer thickness $d_{111} = 0.235$ nm.

Next we turn to the extraction of the model parameters of the Fuchs-Sondheimer theory. This was done with the full Fuchs theory expression,[2-4] with the approximation of Eq. (1), and with the thin-film limit $(d/l \ll 1)$ approximation,[2-4]

$$\rho_0(d) = \rho_\infty \frac{4}{3} \frac{1-p}{1+p} \frac{l/d}{\ln(l/d)} . \tag{2}$$

The fit with the integral or series expression of the full Fuchs theory required considerable computer time and was not significantly better than that of Eq. (1). Therefore, only the simpler fits with Eqs. (1) and (2) were made. The least-squares fit with Eq. (1) is illustrated in Fig. 4 for two arbitrarily selected films. The resulting fit parameters $(1-p)l$ and ρ_∞ are listed in Table I together with the graphically determined fit parameters l and $[(1-p)/(1+p)]\rho_\infty$ of Eq. (2). The relative differences $[\rho_f(d) - \rho_0(d)]/\rho_0(d)$ using Eq. (1) for $\rho_0(d)$ are shown in Fig. 1(b) and Fig. 3 for samples 1 and 2, respectively. The ρ_∞ values are significantly larger than the value for bulk Au of about 0.55 $\mu\Omega$ cm at 95 K which is to be expected because of the small grain size of the Au crystals mentioned above. The mean free path l is in all cases much larger than the film thickness so that scattering on the film boundaries is a dominating factor.

The variation of the specularity parameter p with the periodic change of the step density causes, according to Eq. (1), the resistivity variation

$$\Delta \rho_f = -\tfrac{3}{8} \rho_\infty l \, \Delta p/d . \tag{3}$$

In a simple two-level picture, minimum step density means maximum RHEED specular beam intensity[16] so

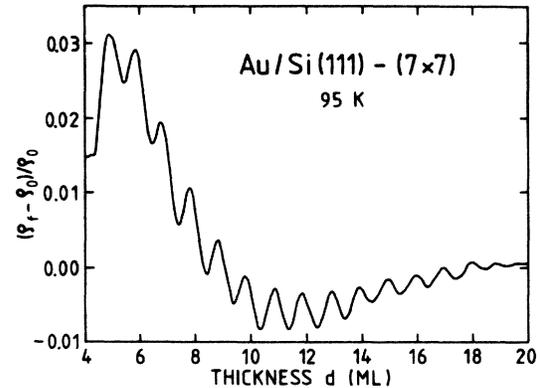FIG. 3. Resistivity oscillations during growth of a Au film on a Si(111)-(7×7) surface at 95 K. Only the thickness region in which the deviation of ρ_f from the Sondheimer approximation [Eq. (1)] is small is shown. The curve was obtained from the upper curve in Fig. 4. The amplitude of the oscillations approaches zero when a steady-state step density is reached at about 20 monolayers.

that the maxima of $p(d)$ and, therefore, the minima of $\rho_f(d)$ in Fig. 1(b) should coincide with the maxima of $I(d)$ in Fig. 1(a). This is nearly though not completely the case in Fig. 1. A certain amount of displacement is actually to be expected because the $I(d)$ maxima rarely coincide precisely with the completion of the monolayer.[14] The essential criterion is, therefore, the good agreement of the periods of $I(d)$ and $\rho_f(d)$.

The absence of $\rho_f(d)$ oscillations in Ag films is in accord with the larger crystal size of these films mentioned before and the structural changes occurring with increasing thickness. Neither the Fuchs formula (1) nor the approximation (2) could be fitted with constant parameters within a reasonable range of the Ag film thickness.

Below 4 ML the fit with Eq. (1) breaks down as seen in Fig. 1(b) and in the lower curve in Fig. 4. This is not due to the approximative nature of Eq. (1) but is also true for the full Fuchs formula. Obviously the Fuchs model is not appropriate any longer. The reason for its failure is not a transition to a discontinuous film which would give a deviation of the measured from the calculated resistivity in a direction opposite to that seen in Fig. 4. Rather, a change of the film structure and/or composition is responsible for the lower ρ_f values. As seen in Fig. 1(a), the RHEED specular beam $I(d)$ oscillations do not become regular up to 3 ML. Furthermore, even beyond 3 ML their amplitudes increase initially up to 6 ML, indi-

TABLE I. Fit parameters of Au films with more than 4 monolayer thickness.

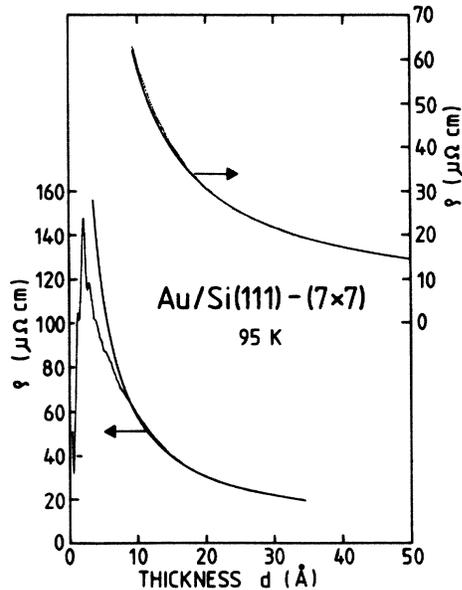|	Eq. (1)		Eq. (2)	
	$(1-p)l$ (nm)	ρ_∞ ($\mu\Omega$ cm)	l (nm)	$\left|\dfrac{1-p}{1+p}\right|\rho_\infty$ ($\mu\Omega$ cm)
Film no. 1	40.8	3.56	37.9	6.1
Film no. 2	35.2	4.03	31.3	7.3

FIG. 4. Experimental (solid line) and fitted theoretical (dotted line) resistivity ρ_f and ρ_0, respectively, of the Au films of Fig. 1 (lower curve) and Fig. 3 (upper curve) deposited on a Si(111)-(7×7) surface at 95 K. The fit was made with Eq. (1).
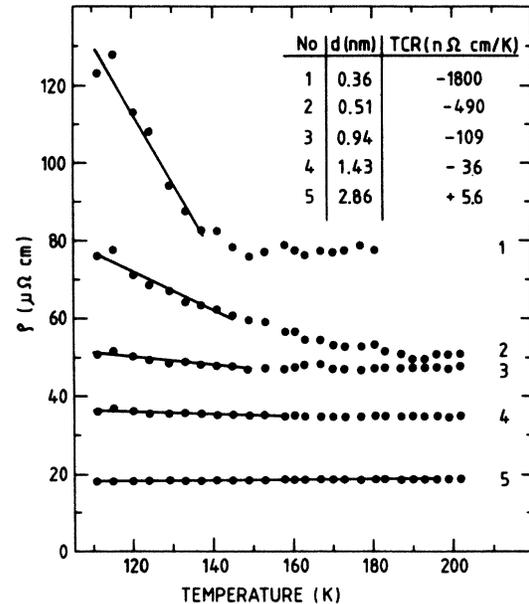

FIG. 5. Resistivity as a function of temperature for a number of samples with different thickness. The inset shows the thickness of the samples and the slopes $\alpha = \Delta\rho/\Delta T$.

cating a transition region from the initial to the final growth. The initial growth is characterized in the RHEED pattern by the disappearance of the Si(7×7) pattern in a strong, diffuse background indicating a disordered film. From this background weak and diffuse Au(111) streaks develop after 3 ML which grow in intensity and sharpen somewhat with increasing thickness.

Further important characteristics of the thinnest films are the following. (i) A maximum of the resistivity at about 1 ML ranging from about 140 $\mu\Omega$ cm in fast depositions to 180–200 $\mu\Omega$ cm in slow depositions. Because of the finite response time of the measurement system the last values are characteristic for the layers. (ii) A negative temperature coefficient of the resistivity (TCR) α below about 6 ML. Due to irreversible changes upon heating above a sample-thickness-dependent temperature T_i, α could be measured only over a small temperature range between 100 K and T_i. Figure 5 shows the dependence of the specific resistivity on the temperature of the sample. The best least-squares fit to the measured points determines the α values shown in the inset and T_i. It is seen that the TCR changes from positive to negative values with decreasing average film thickness d at $d_0 \approx 2.5$ nm, reaching values as high as 1.8 $\mu\Omega$ cm/K for the 1.5-ML Au sample. Similar but smaller changes with the thickness of the individual layers have been reported[17] for Nb/Cu superlattices, with α changing sign at $d_0 \approx 1$ nm. The α and ρ values are not compatible with the Mooij correlation which states that $\alpha > 0$ for $\rho < 100$ $\mu\Omega$ cm in disordered alloys.[18] Here the lowest ρ value for which $\alpha < 0$ was 35 $\mu\Omega$ cm at 6 ML. Thus a Au-Si alloy which had been suggested by Demuth et al.[19] as the cause of the abnormally high resistivity of an 0.85-nm-

thick Au film deposited at room temperature on a Pd-impurity-stabilized Si(111) surface appears unlikely in our case, in particular as the TCR is still negative in the range of the regular $I(d)$ oscillations.

The maximum resistivity observed in our samples, 200 $\mu\Omega$ cm, may be compared with the value predicted by the Mott-Ioffe-Regel rule.[6] This rule is derived from the assumption that the minimum mean free path l_{min} is equal to the interatomic distance a. This results in a maximum resistivity $\rho_{sat} = (3\pi^2)^{1/3}\hbar/e^2 n^{2/3}a$, where n is the electron concentration.[20] For Au one obtains with $n = 1.506 \times 10^{23}$ cm^{-3}—assuming one electron per atom—and $a = 0.288$ nm, $\rho_{sat} = 297$ $\mu\Omega$ cm. The lower values obtained here together with the negative TCR may be considered as a sign of localization. The data for less than 6 ML of Au—and similarly those for the first few ML of Ag—will, therefore, be evaluated elsewhere within the framework of the theoretical models of weak localization and electron-electron interaction.[1,6]

IV. CONCLUSIONS AND SUMMARY

We have shown that ultrathin continuous single-crystal films of Au and Ag with good surfaces can be grown at about 100 K on carefully prepared Si(111) surfaces by combined UHV in situ measurements of resistivity, thickness, and growth behavior with RHEED, in particular of the specular beam intensity. This combination allowed us to correlate periodic resistivity oscillations in Au films with oscillations of the specularity of the electron scattering on the growing surface of the film, caused by oscillations of the density of surface steps. The absence of resistivity oscillations in Ag films could be attributed to the

higher perfection of Ag surfaces as seen by RHEED. Although both films were atomically smooth according to RHEED, no quantum size oscillations could be seen. This casts some doubt on the interpretation of irregular conductivity oscillations of much rougher polycrystalline Pt films in terms of quantum size effect.[21]

Au and Ag layers differ not only in their perfection as determined by RHEED but also in other aspects. (i) In contradiction to Au, the Ag data could not be fitted with Fuchs-Sondheimer theory with constant parameters within the thickness up to 13 nm confirming structural changes occurring during the film growth. (ii) Ag grows monolayer by monolayer from the very beginning while the first three layers of Au are disordered. Although initial gold silicide formation cannot be excluded unambiguously our experimental data speak against it. Below 6 ML the resistivity curve of Au deviates increasingly from the Fuchs-Sondheimer theory. An increasingly negative TCR and a resistivity maximum signal a crossover from 3D to 2D conduction and a transition to localization. The first few monolayers, therefore, promise to be an ideal testing ground of localization and interaction theory.[6]

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