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Metallic and nonmetallic conductivity of thin epitaxial silver films

R. Schad, S. Heun, T. Heidenblut, and M. Henzler
Universität Hannover, Institut für Festkörperphysik, Appelstrasse 2, 3000 Hannover 1, Germany
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The conductivity of thin epitaxial Ag films on Si(111) surfaces is studied as a function of film thickness [0–125 monolayers (ML)] and temperature (20–300 K) under ultrahigh vacuum conditions. Different regimes of conductance can be distinguished. Films thicker than 2 ML behave metallically with small corrections due to weak localization effects. The thickness dependence of the elastic mean free path is given by electron scattering at the surfaces and at bulk defects. The electron states in films thinner than 2 ML are obviously localized. The conductance measured during the deposition of Ag on Si(111) at 50 K may be described in terms of a two-dimensional percolation problem.

The conductance of metals is usually described by their conductivity and the dimensions. Very early it was found that the mobility of the carriers is reduced by surface scattering as soon as the dimension (diameter of a wire or thickness of a film) becomes comparable with the mean free path of the carriers between scattering events.[1] More recently also quantization effects have been detected for very thin films or wires especially at low temperatures due to interference effects.[2] In most experiments fairly thick films (10–100 nm) have been used, since for thinner films the roughness of the substrate and the inhomogeneity of the film itself may prevent a smooth or even continuous and coherent film.[3] To study the effect of two-dimensional (2D) conductance in much thinner films down to a metallic monolayer, first a substrate has to be found with an asperity height less than atomic distance. Here the Si(111) surface with 7×7 superstructure has been shown to provide the best surface with respect to steps, point defects, and domain boundaries, especially since crystals are dislocation free only for Si.[4] The second requirement is a film which grows epitaxially on Si(111). Several metals like Au, Ag, and Pb are suited. Already some conductivity measurements are available.[5,6] But measurements at low temperatures with well-defined epitaxial structure are still missing. It is therefore the purpose of this paper to study the conductivity of epitaxial Ag films on Si(111). The films are grown on well-annealed Si(111) surfaces in the thickness range of 1–125 monolayers (ML).

All preparations and measurements were done in a UHV system (base pressure 5×10^{-11} mbar) as described elsewhere.[7] The silver was evaporated from a resistively heated tungsten filament with a rate of 0.1 ML per min. Even during the deposition the pressure stayed below 1×10^{-10} mbar. The substrates are squares of Si(111) wafers with contact areas in the corners and notches on each side. The conductance is measured and evaluated according to van der Pauw.[8] Special care has been taken to prepare a substrate with both a low conductivity and good contacts even to the thinnest metal films. To increase the resistivity of the wafer (originally $\rho=500\ \Omega$ cm) a monolayer of Au has been deposited onto the clean Si(111) surface in UHV, which after annealing produces a conductance of less than 50 nA/V < 50 K via bulk doping ($\approx10^{16}/\mathrm{cm}^3$). Before mounting, the contact areas were formed by deposition of 100-nm Mo and annealing to silicide at 450 °C. After mounting, the samples were heated in UHV up to 1300 °C in order to form a clean, step-free surface with a 7×7 superstructure with sharp low-energy electron-diffraction (LEED) spots in the center portion. The LEED pattern is not affected by the Au doping. To ensure a good contact between the Mo contact areas and even very thin films, 20 ML of Ag were deposited onto the whole sample and removed from the center portion by heating. After this procedure neither Ag, Au, nor Mo were detectable on the center of the sample by means of Auger electron spectroscopy, just a bright 7×7 LEED pattern. So the films could be deposited onto clean Si(111)-7×7 and contacted by the Ag on the contact areas. The film thickness was monitored by a quartz microbalance, which has been calibrated by comparing the measured temperature coefficient of the resistivity of thick Ag films (> 100 ML) with bulk literature data.[9] Conductivity measurements were done during deposition at temperatures down to 50 K. Due to an additional radiation shielding the conductivity was measured after deposition in the range 20–300 K without breaking the vacuum. The conductivity of Ag films with thickness from 1 to 125 ML has been measured at $T=20$ K. Immediately after deposition at 50 K the conductance is increased by annealing up to a maximum value before breaking up into islands (Fig. 1). The temperature for optimum conductance is higher the thicker the film is. The temperature dependence of conductivity after annealing reveals many details of scattering mechanisms (Fig. 2). The 6-ML-thick film shows a change of sign of the slope. To check the onset of conductivity the conductance of the substrate and the film has been measured during deposition at 54 K (Fig. 3). Even for coverages less than a monolayer a conductance of the film is well resolved. However, we never measured oscillations of the conductance during growth (due to quantum size effect[6] or oscillation of the surface roughness[5]).

The low-temperature conductivity may be evaluated by scattering in a first approximation via the Drude formula $\sigma=ne^2\tau/m$ (using a carrier density of one electron per atom, the free electron mass m and scattering time $\tau=l/v_{\mathrm{Fermi}}$ to derive an elastic mean free path l as shown

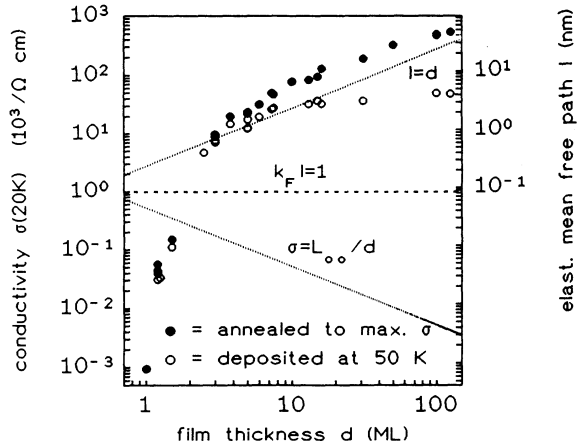

FIG. 1. Conductivity and elastic mean free path, l, vs film thickness d measured at $T=20$ K. Shown are two sets of data: ○, films immediately after condensation at $T=50$ K; ●, the same films after annealing to maximum conductivity. The horizontal dashed line indicates $k_F l=1$, a lower limit for l related to the Ioffe-Regel criterion. The dotted lines show the conductivity for a film of the given thickness with a conductance $L_{00}=e^2/2\pi^2\hbar$ (lower limit for extended electron states).

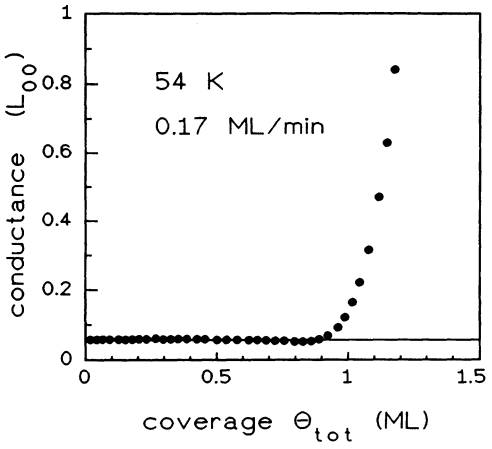

FIG. 3. Conductance of a sample (in units of $L_{00}=e^2/2\pi^2\hbar$) vs thickness of deposited Ag at a substrate temperature of 54 K. The conductance for zero coverage is due to the substrate conductance (illuminated by the evaporator). The threshold of beginning conductivity of the Ag layer is 0.9 ML.

on the right-hand side of Fig. 1. The elastic mean free path should always be larger than the interatomic distance. This condition is usually expressed by the Ioffe-Regel criterion $k_F l > 1$,[10] and is indicated in Fig. 1 by the horizontal dashed line. The discussion is therefore different for films thicker or thinner than 2 ML.

Films thicker than 2 ML. Although the conductivity of the films with the highest conductivity (125 ML, annealed) is about 2 orders of magnitude smaller than the conductivity of bulk silver,[9] the charge transport in all films thicker than 2 ML can be understood in terms of a metallic film with strongly increased defect density. For all of these films the Hall effect (at $T=20$ K) shows the bulk charge density. All silver bulk band-structure features are clearly seen in photoemission for films of at least 2 ML thickness.[11] The magnetoresistance shows classical behavior ($\sigma=\sigma_0[1-(\omega_c\tau)^2]$, $\omega_c=eB/m$) for films with 100 ML. The magnetoresistance is modified for films of 2–16 ML due to weak localization (to be published in a forthcoming paper). The temperature dependence of the conductivity (Fig. 2) is typical for a metal for thick films ($d>7$ ML) with a residual resistance at low temperatures depending on defects and a resistivity increase with increasing temperature independent of defects and equal to the bulk value.[9] Thinner films show a change in the sign of the temperature coefficient. At a coverage of 6 ML the conductivity has a maximum at 40 K which can be described within the model of weak localization.[2] The conductivity of films with coverage in the range of 2–5 ML increases with temperature in a wide temperature range, a phenomenon which has been called incipient localization.[12] The elastic mean free path l may be described by two effects: bulk scattering and surface scattering. The bulk scattering is due to growth defects in the film, which are partially annealed during heat treatment. The conductivity of the freshly deposited film is limited by a mean free path of a few nanometers, whereas after annealing an increase to some 10 nm is observed. The combination of the two scattering processes describes the observed mean free paths in Fig. 1 well. A flat metal surface is expected to reflect the conduction electrons in a specular way so that conductivity is not reduced.[13] Therefore the corrugation of the 7×7 structure at the interface may be the reason for diffuse scattering. Also for the Si(111)-$\sqrt{3}$ Ag interface a specular scattering is reported.[14] Systematic variations of the interface with respect to interface scattering are in progress.

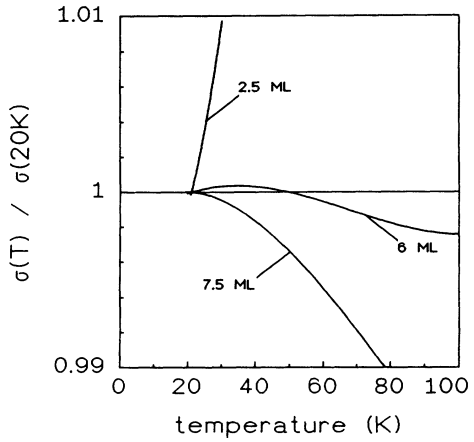

FIG. 2. Normalized conductivity vs temperature for different film thicknesses after annealing to maximum conductivity. The absolute values at 20 K are σ(2.5 ML) = 4700/Ω cm, σ(6 ML) = 40 800/Ω cm, and σ(7.5 ML) = 47 700/Ω cm.

Films thinner than 2 ML. The mean free path, as derived from Drude's formula and shown in Fig. 1, is for thin films less than atomic distances and below the value of the Ioffe-Regel criterion $k_F l=1$. The interpretation as a mean free path between scattering events does not apply

anymore. Nevertheless, using carrier density and mobility for a description of conductivity one may ask which quantity is reduced. The mobile carrier density should be reduced according to a recently published calculation[15] revealing a band gap at the Fermi level in the band structure of one or two perfect (111) layers of noble metals. Our Hall effect data do not show a decrease of carrier density at low temperatures to account for the conductance as observed. So the transport has to be described with a mobility fulfilling the following properties. The transport is not diffusive—rather, it is via localized states, which is consistent with the conductance lower than the universal conductance $L_{00}=e^2/2\pi^2\hbar$ as the lower limit of extended electron states.[16] An additional feature is the increase of conductivity with temperature, which may hint to an activated transport. Unfortunately, the present data do not yet allow one to distinguish between an $\exp(T^{-1/4})$ law for variable range hopping[17] and an $\exp(T^{-1/2})$ law for hopping with an additional Coulomb gap.[18] Although a full analysis still has to be done, the disorder of the very thin films may cause strong localization for the electrons.

Another topic of interest is the onset of conductivity during deposition of Ag (Fig. 3). In the simplest model a triangular percolation system requires only 0.5 ML for the first conducting path.[19] Observed is a coverage of 0.9 which uses the observed lattice constant of the Ag film [equal to a bulk Ag(111) plane]. This discrepancy may be explained in different ways. The first possibility is that it is due to the growth mode. During deposition some atoms may be found in the second level if they arrive on top of an already formed Ag island. If a higher substrate temperature is chosen, then this effect should be smaller due to a higher mobility of the Ag atoms, which may cross the island edges for deposition into the first layer. This model is supported by an experiment at $T=94$ K. Here the first conductivity increase was observed already at a coverage of 0.75 ML. The high-resolution LEED experiments in progress should clarify if this model is applicable. A second model asks for specific conductance properties close to the percolation limit. Since one or two monolayers have a conductivity lower than the bulk by several orders of magnitude, additional reductions may occur, when besides vertical limitations a narrow path with a width of a few atoms is also needed for a dc conductivity. Further experiments in that coverage regime at different temperatures with and without magnetic field should help to clarify this question. The present results already reveal that an epitaxial monolayer of Ag has a dc conductivity. The details of the transport mechanism, however, are still open.

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