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Growth and structure of Ag on Pd(111) studied by photoelectron forward scattering using a two-dimensional display-type analyzer

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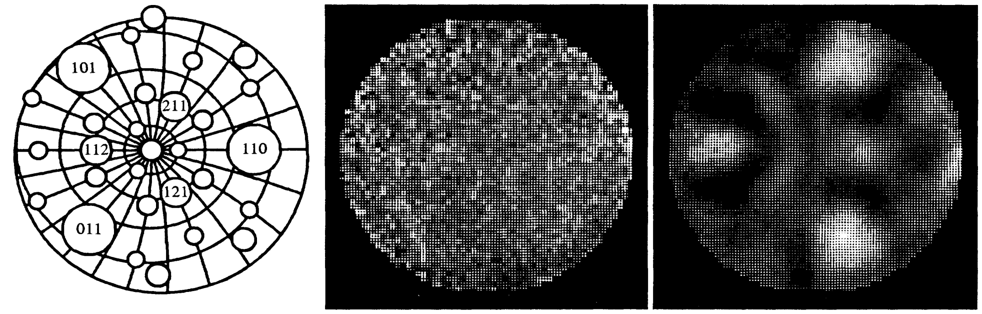
For an investigation of the growth and the structure of thin Ag films on Pd(111), the angular distribution of core-level photoelectrons emitted at high kinetic energy (>500 eV) was measured with a two-dimensional display-type electron spectrometer. At room temperature, Ag grows epitaxially on Pd(111) in the layer-by-layer mode. The Ag films have fcc crystal structure and grow with a stacking fault at the interface relative to the Pd(111) substrate. Low-energy electron-diffraction-intensity measurements show that the first Ag layer is pseudomorphic with the Pd(111) substrate and the stacking fault occurs between the first and the second Ag layers.

Thin metal films on single-crystal metal surfaces differ frequently in mechanical, electronic, and magnetic properties from their bulk materials. One important step in understanding these unusual properties is the determination of the growth and the structure of these films. A method that is able to give information on both growth and structure is the new technique called photoelectron forward scattering.[1] This method uses the fact that photoelectrons with a kinetic energy of some hundred electron volts exhibit enhanced intensity along the internuclear axes connecting the emitting atom with its neighbor atoms due to forward scattering. The angular distribution of these photoelectrons yields, therefore, structural information. Since photoelectron spectroscopy is, furthermore, an element specific method, the observation of the angular distribution of the core-level photoelectrons constitutes a probe of short-range order around a particular element within the surface region. This technique combines, therefore, structural sensitivity and chemical selectivity, properties that are particularly useful for studying epitaxial overlayer systems. In order to obtain the complete structural information, however, the measurement of the whole angular distribution is required. In this work we use a two-dimensional display-type electron spectrometer,[2] which allows us to measure simultaneously the complete angular distribution of photoelectrons in an acceptance cone with an 88° opening. The time for recording the angular distribution is reduced by approximately two orders of magnitude compared to conventional electrostatic energy analyzers. To demonstrate the applicability of the forward-scattering experiment using a two-dimensional display-type analyzer we have investigated Ag films on Pd(111). Up to now only two investigations of Ag films deposited at room temperature on Pd(111) exist.[3] These studies using Auger electron spectroscopy (AES) have been restricted to the determination of the growth mode of the Ag films. Weak bents in the Auger electron intensity versus coverage curve were used to derive the layer-by-layer growth mode of the Ag films on Pd(111).

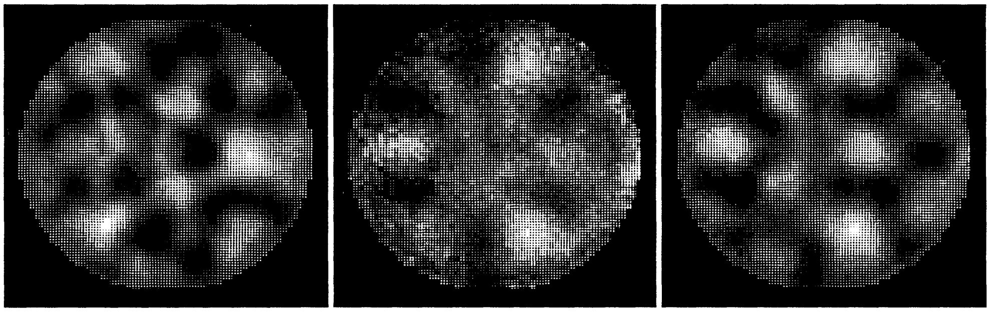
In our photoelectron forward-scattering experiment synchrotron radiation with an energy of 900 eV from the HE-TGM-1 beam line at the Berliner-Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung storage ring was employed to excite the $3d$ core levels of Ag and Pd. The original angular distribution patterns (ADP's) have to be corrected for the background of inelastic electrons and for the spatial analyzer efficiency due to the inhomogeneities mainly caused by the nonlinear amplification of the microchannel plates. For background correction ADP's were measured at the kinetic energy of the core level and an ADP measured at 10 eV higher kinetic energy was subtracted. The spatial analyzer efficiency is obtained in the following way: ADP's were measured for 20 s each at 13 azimuthal positions (8° apart) of the sample. In this way the intensity maxima are swept over the detector area. The sum of these 13 ADP's yields, therefore, the spatial sensitivity of the analyzer and is used to normalize the ADP's shown in Fig. 1. An ADP is composed of 64×64 pixels. For bulk Pd(111) in 96 s an average of about 9600 electrons is collected in each of the illuminated pixels. ADP's are presented in form of gray-scale pictures. In order to improve the contrast of the ADP's we always used the whole gray-scale range, i.e., the highest intensity is shown as white and the lowest as black.

The low-energy electron-diffraction (LEED) measurements and the sample preparation have been done in a separate chamber which is connected by a transfer system with the analyzer chamber described previously.[2] LEED intensity measurements [$I(E)$ curves] were recorded with a commercial four-grid optic in combination with the image processing system of the display-type electron spectrometer. The sample was cleaned by Ar^+ sputtering and heating followed by repeated oxidation and heating cycles to 900 K to remove residual carbon. The sample preparation was checked with AES, thermal-desorption spectroscopy, and LEED. Ag was evaporated from a tungsten basket at a rate of 0.01 monolayers (ML) per second onto the Pd(111) substrate at room temperature and at a pressure of $<2\times10^{-10}$ mbar. The coverage was controlled by means of a quartz microbalance and calibrated by AES measurements.

In Fig. 1(a) the expected angular distribution of photo-



(a) (c) 1.0 ML Ag/Pd (e) 3.0 ML Ag/Pd



(b) Pd(111) (d) 1.8 ML Ag/Pd (f) 4.0 ML Ag/Pd

FIG. 1. (a) Expected angular distribution of photoelectrons for a fcc (111) surface due to the forward scattering of the electrons by the neighbor atoms along the crystal directions given by the numbers. The separation between the lines of the grid are 10° and 15° for the polar and azimuthal directions, respectively. (b) Experimental angular distribution of $3d$ photoelectrons (kinetic energy 548 eV) from a Pd(111) crystal. The intensity increases from black to white. (c)–(f) Experimental angular distributions of $3d$ photoelectrons (kinetic energy 520 eV) for Ag films deposited at room temperature on Pd(111). The Ag films grow in a layer-by-layer fashion with a stacking fault relative to the Pd(111) substrate.

electrons for a face-centered-cubic (fcc) (111) surface calculated with a simple forward-scattering model (see Fig. 2) is shown. The area of the circles represents roughly the expected intensity which is assumed to decrease with the square of the reciprocal distance between the emitter and the scatterer. The numbers give the crystal directions between emitter and scatterer. The experimental ADP of clean Pd(111) shown in Fig. 1(b) agrees with the expected angular distribution from the simple forward-scattering model [Fig. 1(a)]. In addition to the intensity maxima in the forward-scattering directions there exist bands connecting the intensity maxima in the $\langle 110 \rangle$ directions. These bands can be interpreted in terms of Kikuchi bands and have been also observed in the ADP's of other fcc metals.[4] The ADP of Pd(111) is a direct image of the directions of the high-density atom chains and planes in real space.

In Figs. 1(c)–1(f) we show ADP's for Ag coverages between 1.0 and 4.0 ML on Pd(111). For 1.0-ML Ag [Fig. 1(c)] the angular distribution of the Ag $3d$ photoelectrons is uniform. So no atomic scatterers can be between the emitting Ag atoms and the detector. This proves, therefore, the growth of a single layer and the absence of islands or alloy formation. Upon deposition of the second silver layer [Fig. 1(d)] enhanced intensity appears along the $\langle 110 \rangle$ directions due to the forward scattering at the nearest-neighbor atoms (see Fig. 2). At 3.0-ML Ag [Fig. 1(e)] additional intensity maxima along the $\langle 211 \rangle$ directions can be observed due to the forward scattering at the next-nearest-neighbor atoms (see Fig. 2). The deposition of 4.0-ML Ag [Fig. 1(f)] causes the development of more spots due to other forward-scattering directions from deeper layers. This sequence of ADP's shows clearly the layer-by-layer growth mode of Ag on Pd(111) in agreement with Ref. 3 and recent two-photon photoemission spectroscopy results.[5]

Thermodynamic considerations allow one to predict the growth mode of a thin film under equilibrium conditions.[6] The requirement for a layer-by-layer growth to occur is that the sum of the film surface free energy plus the interfacial energy must be smaller than the substrate

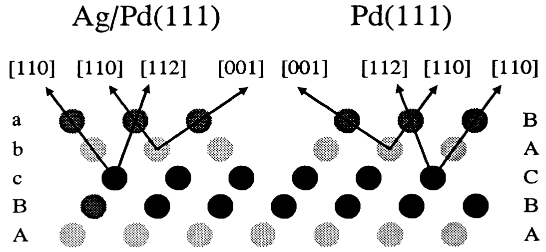


FIG. 2. Illustration in the $(1\bar{1}0)$ plane of the stacking fault during the growth of thin Ag films on Pd(111). The intensity maxima in the ADP's correspond to the low-index crystallographic directions.

surface free energy.[6] The surface free-energy values for Pd(111) and Ag(111) are 1.22 and 0.62 J/m^2 (Ref. 7), respectively. The interfacial energy contains a chemical and a structural component.[8] For the first Ag layer the sum of both components can be estimated to -0.55 J/m^2.[7,9] Consequently, the layer-by-layer growth mode is expected in accordance with our photoelectron forward-scattering results.

The forward-scattering experiment with full-angle display, furthermore, allows the determination of the symmetry, the orientation, and the stacking of the film. The ADP of 4.0-ML Ag on Pd(111) shows basically a threefold symmetry.[10] This enables us to conclude that the Ag film has the fcc lattice structure. Comparing the ADP of 4.0-ML Ag with the ADP of Pd(111) we observe the spots just reflected at the $(11\bar{2})$ plane relative to the corresponding spots of the clean surface. This can be easily seen by the triangle spanned by the three intensity maxima in the $\langle 110 \rangle$ directions. In the case of Pd(111) the triangle points to the right, whereas for 4.0-ML Ag it points to the left. This proves unambiguously the different stacking of Ag relative to the Pd substrate. In order to illustrate the stacking fault at the interface Fig. 2 shows a view of the $(1\bar{1}0)$ plane. For Pd(111) the regular stacking of the fcc crystal (*ABC*) is preserved and the [110] direction points to the right. In contrast to that the stacking of Ag on Pd(111) is *cba*. So the regular stacking of the fcc crystal is no longer continued near the interface and a stacking as in a hcp crystal occurs similar to a fcc twin. Consequently, the [110] direction now points to the left. As shown in Fig. 1(d) the 1.8-ML Ag film already has dominantly the hcp orientation relative to the Pd substrate. Since the ADP of 1.0-ML Ag is uniform, the angular distribution of Ag 3*d* photoelectrons yields, however, no information whether the stacking fault occurs between the top layer of the Pd substrate and the first Ag layer or between the first and the second Ag layer.

To answer this question we have performed LEED-intensity measurements. Figure 3 shows the experimental $I(E)$ curves (integrated intensities) of the (1,0) and $(\bar{1},0)$ spot in comparison with LEED-intensity calculations for 1.0-ML fcc and hcp Ag on Pd(111). The best agreement between the experimental and calculated curves was found for the fcc orientation with the in-plane lattice constant of Pd(111) and the first interlayer spacing of 2.35±0.05 Å which corresponds to the value of bulk Ag(111). The first layer of the Ag film conforms to the lattice structure of the Pd(111) substrate, i.e., is pseudomorphic with the Pd(111) surface. The stacking fault must occur, therefore, between the first and the second layer of the Ag film. For Ag coverages between 1.5 and 2.0 ML on Pd(111) the LEED spots are split in a fashion comparable to that observed for the $(23\times\sqrt{3})$ reconstruction of the Au(111) surface.[11] At higher Ag coverages (even for the thickest Ag film grown in this work of 20 ML) the LEED pattern is (1×1) with slightly broader spots and higher background as compared to the clean Pd(111). LEED-intensity measurements and calculations performed for 9.6-ML Ag on Pd(111) confirm the results of the forward-scattering experiment that the Ag film has the fcc crystal structure of bulk Ag(111) and grows as a fcc twin relative to the Pd(111) substrate.

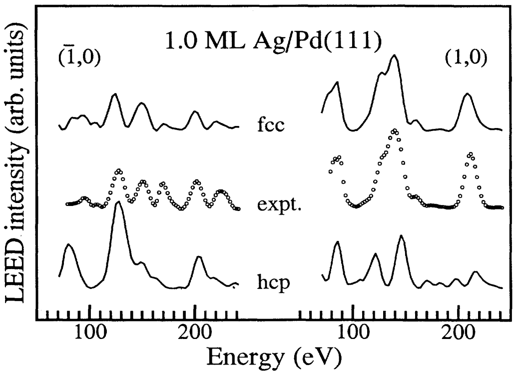


FIG. 3. Experimental and theoretical LEED $I(E)$ curves for a 1.0-ML Ag film on Pd(111) at normal incidence of the primary electron beam. The calculations are for 1.0-ML Ag in fcc and hcp orientation relative to the Pd(111) substrate with the in-plane lattice constant of Pd(111). The agreement between the experimental and the theoretical curves proves the pseudomorphic growth of the first Ag layer.

Theories of epitaxial growth estimate the equilibrium value of the largest lattice mismatch that still allows a pseudomorphic growth with monolayer thickness to about 5.3%.[12] Experimentally, however, pseudomorphic growth has been observed even for a lattice mismatch of 7.8% on Cu/Pd(001).[13] Since the lattice mismatch due to the different lattice constants of Ag and Pd is 4.9%, the pseudomorphic growth of the first Ag layer is reasonable. The stacking fault between the first and the second Ag layer occurs in order to accommodate the lattice mismatch between Pd and Ag. Details of this process will be presented in a more extensive paper.

A stacking fault seems to occur also during the growth of Ag on other fcc substrates as can be seen by comparison of our ADP's of Ag films on Pd(111) to the ADP's of Ag films on Pt(111) (lattice mismatch 4.2%) measured by Hubbard *et al.*[14] The ADP's of Ag on Pt(111) suggest that the Ag films grow also with a stacking fault relative to the Pt(111) substrate. The accommodation of the lattice mismatch for both systems is probably similar.

In summary, the forward-scattering experiment yields a wealth of information about the growth and the structure of thin films on single crystal surfaces which can be obtained by a straightforward interpretation of the ADP's without any calculation. These ADP's can be measured very fast with our two-dimensional display-type electron spectrometer. We have investigated recently the growth and the structure of thin Au films on Pd(111) and Ag(111) by forward-scattering experiments.[15]

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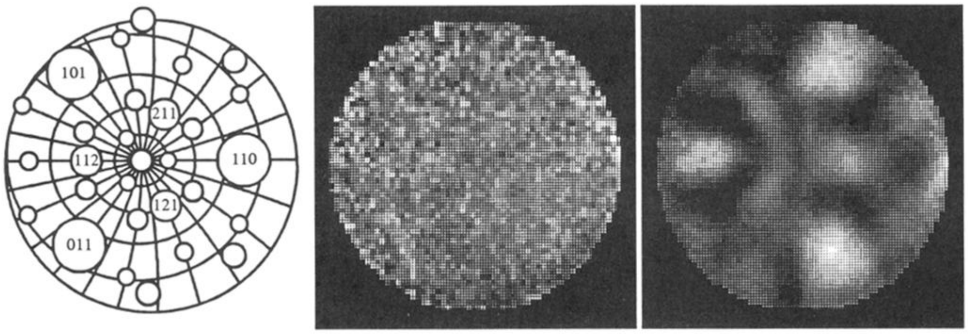

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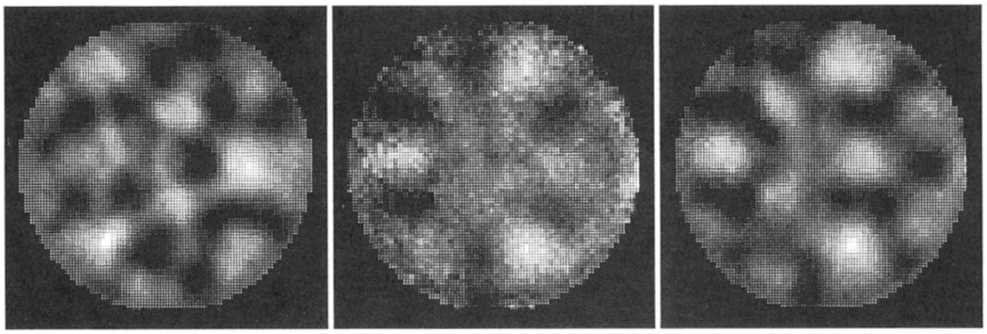

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