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Properties of Pt on Cu(111) revealed by AES, LEED, and DEPES

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ABSTRACT

The investigations of Pt on Cu(111) were carried out to reveal the growth mode and crystalline structure of the adsorbate with the use of Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and directional elastic peak electron spectroscopy (DEPES). Auger signal recorded during the continuous Pt adsorption on Cu(111) at 330 K confirms the layer by layer growth mode. LEED patterns observed at 1ML of Pt show the formation of the compressed adlayer. At higher coverages such as 3ML and 6ML the increase of the lattice constant of the topmost Pt layer, which approaches the bulk value of Pt(111), is noted. DEPES investigations performed for 1ML of platinum indicate the nucleation of adsorbate domains characterized by A/CBA and B/CBA stacking sequences at the Pt/Cu interface, which at higher coverages lead to the nucleation of mutually rotated by 180° Pt islands. Experimental DEPES data were compared to theoretical results obtained with the use of the multiple scattering (MS) calculations for different adsorption geometries including the Pt and Cu intermixing at the interface. The quantitative analysis of the data made by R-factor calculations enabled the determination of Pt domain populations already at 1 ML and 6 ML.

1. Introduction

Understanding of processes occuring on solid state surfaces is crucial for basic science and is a key for knowledge based technology. The structure and composition of surfaces determine their properties, which can lead to industrial applications in e.g. heterogeneous catalysis. The bimetallic systems often exhibit different properties from their individual components, therefore focused attention of researchers [1,2,3]. The change of the local neighborhood of surface atoms is associated with the breaking or formation of bonds, which results in the modification of the electronic structure. In this context the enhanced selectivity, activity and stability of catalysts is of great importance. Exemplary investigations of the Cu-Pt system associated with the hydrogenolysis of pentane and hydrocarbon reforming reactions are reported in [4,5]. Further investigations of the crystal growth, its crystalline and electronic structure, as well as composition of binary system surfaces are desirable.

One of the frequently investigated bimetallic systems is Pt/Cu(111). A number of experimental methods such as: medium energy ion scattering (MEIS) [6,7], low energy electron diffraction (LEED) [6], thermal desorption spectroscopy (TDS) [8], Auger electron spectroscopy (AES) [9], reflection high energy electron diffraction (RHEED) [9], photoelectron spectroscopy (PES) [10,11], x-ray photoelectron diffraction (XPD) [10], and scanning tunneling microscopy (STM) [12] were used to characterize its properties. This system was also addressed theoretically by the application of density functional theory (DFT) [13,14], and Bozzolo-Ferrante-Smith (BFS) method [15].

The Pt/Cu system is characterized by about 8% lattice mismatch, which leads to the strain at the interface. A layer by layer growth mechanism of Pt on Cu(111) was reported at room temperature [9,16]. Platinum forms an epitaxial overlayer on Cu(111) with face centered cubic (fcc) stacking sequence [16]. The exothermic heat of mixing favors the Pt-Cu alloy formation, which can exist in three bulk phases of different stoichiometry: $CuPt_3$, CuPt, and Cu_3Pt [17]. Ion scattering experiments clearly indicate the formation of the stable $Cu_3Pt(111)$ alloy phase, which extends within first few monolayers, after annealing above 550 K [6,7]. The formation of the step mediated precursor alloy was reported to take place even at lower deposition temperatures such as 225 K [7]. The Cu_3Pt composition of the surface layer was also confirmed by PES experiments [10]. The ideal (111) surface of the Cu_3Pt monocrystal exhibits a $p(2 \times 2)$ structure of the Pt atoms. The (3×3) R30° arrangement of Pt atoms characterizes the $Cu_2Pt(111)$ surface. The recent STM investigations performed after annealing at 315 K show that the Pt-Cu intermixing occurs mainly due to the place exchange at step

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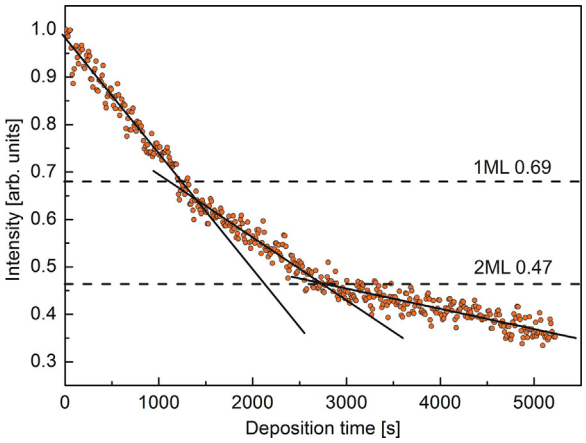

Fig. 1. Auger signal intensities of the Cu 922 eV peak normalized to the signal from the clean substrate as a function of the deposition time of Pt on Cu(111) at the substrate temperature of 330 K. Calculated signal values from copper at 1ML and 2ML Pt coverages are given (dashed lines).

edges [12]. DFT calculations confirm the formation of the energetically favored pseudomorphic monolayer surface alloy [13].

Although the structural investigations of Pt on Cu(111) performed with the use of LEED and XPD have been already reported in the literature [10], the detailed picture of the crystal growth, crystalline structure at different Pt coverages, from early stages of growth till few monolayers, is still missing. Therefore, in this work we present the results of structural investigations, which concern the long and short range order revealed by LEED and directional elastic peak electron spectroscopy (DEPES) [18,19], respectively, as well as the chemical composition and growth mode studied by AES. Forward scattering of primary electrons makes DEPES a very sensitive toll for the determination of the atomic arrangement within a unit cell of first few atomic layers. The DEPES experimental data supported by the results of numerical calculations performed with the use of the multiple scattering (MS) formalism [20] provide very useful quantitative information concerning e.g. the lattice parameters [21,22], adsorption sites of adatoms [23], and identification of adsorbate domains exhibiting different orientation, which results from different stacking sequences at the interface [24]. Moreover, the formation of the surface alloy at first stages of adsorbate growth can be proved by the quantitative analysis of DEPES data.

2. Experiment

All experiments were carried out in an ultra high vacuum (UHV) apparatus at residual gas pressure lower than 1×10^{-8} Pa. AES spectra, LEED patterns, as well as DEPES distributions were recorded with the use of a standard four grid retarding field analyzer (RFA) with the acceptance angle of 110°. The Cu(111) monocrystal was cleaned using argon ion sputtering and repetitive cycles of annealing at temperature around 1200 K controlled by a thermocouple. The cleanliness of the sample was monitored by AES. The AES spectra, as well as peak to peak Auger signal intensities h_{Cu} of Cu (922 eV) were recorded in a differential dN(E)/dE mode, by measuring of the second derivative $d^2I(E)/dE^2$ of the collector current with the use of a lock-in amplifier, during the continuous evaporation of Pt at sample temperature of 330 K. In this way the growth mode of the adsorbate was determined. Platinum was evaporated from the calibrated Knudsen cell at constant deposition rate. The DEPES measurements were performed in a normal N(E) mode, by recording of the first derivative dI(E)/dE of the collector current. The sample was mounted on a precise manipulator, which enabled the sample annealing and rotation around the polar axis parallel to the sample surface and azimuthal axis perpendicular to its surface. In DEPES the current of elastically backscattered electrons was recorded as a function of the incidence angle of the primary electron beam at electron energies of 0.8 keV and 1.1 keV. The polar profiles were recorded by the change of the polar angle in the range of $+/- \theta_{max}$ with the $\Delta\theta = 0.25°$ step for different azimuthal angles φ changed from 0° to 180° with the $\Delta\varphi = 2°$ increment. The DEPES data were presented in a form of $I(\theta,\varphi)$ stereographic projections with the use of the coordination transfer function $x = 2tg(\theta/2)\sin\varphi$ and $y = 2tg(\theta/2)\cos\varphi$. Because of the threefold symmetry of the Cu(111) substrate the intensities within experimental DEPES distributions were averaged by the symmetrization procedure. All intensities within each DEPES distribution were normalized to the signal value at the normal incidence (θ=0°) and scaled by color. In order to reveal the details of intensity features observed in DEPES distributions for Pt adlayer on Cu(111) the background subtraction procedure was applied [25].

3. Results and discussion

The growth mechanism of Pt on Cu(111) at 330 K was investigated by recording of the Auger signal from the substrate during the continuous Pt adsorption (Fig. 1). The results indicate three regions associated with the formation of subsequent Pt layers. The calculated values of the Auger signal from the substrate at 1ML and 2ML Pt coverages are indicated by the dashed lines. In calculations the Pt layer thickness and inelastic mean free path value [26] of Auger electrons from Cu (922 eV) in Pt overlayer were taken into account. All experimental and theoretical signal values were normalized to the signal from the clean substrate. The obtained theoretical signal ratios $h_{Cu/1ML}/h_{Cu,0ML} = 0.69$ and $h_{Cu/2ML}/h_{Cu,0ML} = 0.47$, where $h_{Cu/XML}$ represents the signal from Cu at X ML Pt coverage, correspond to the characteristic breaks noted in Fig. 1. This result confirms that Pt growths on Cu(111) in a layer by layer manner at early stages of growth, which supports the conclusions of earlier publications [9,16].

The long range order within the adsorbed layer was monitored by LEED. The sequence of LEED images recorded for the clean and Pt covered substrate at 185 eV is shown in Fig. 2. All patterns exhibit characteristic for the fcc (111) surface symmetry. At 1ML the spot distribution is almost identical as for clean Cu(111), which suggests the formation of a compressed Pt monolayer as also reported in the literature [9,16]. At higher coverages such as 3ML and 6ML the slight contraction of diffraction spots towards the (00) reflection is noted (Fig. 2d), which indicates the increase of the lattice constant of the topmost Pt layer. At 6ML coverage the separation of reflections scales with the nearest neighbor Pt–Pt distance of the Pt(111) surface.

In order to reveal the short range order within the first few sample layers the DEPES method was applied. In Fig. 3 the experimental and theoretical DEPES distributions, the later calculated with the use of the multiple scattering formalism [20], obtained for Cu(111) at the primary electron beam energy $E_p = 0.8$keV, are shown together with the stereographic projection of the fcc (111) crystal. The intensity maxima correspond to the close packed rows of atoms such as ⟨110⟩, ⟨112⟩, ⟨114⟩, and ⟨001⟩. The theoretical distribution reflects main features observed experimentally.

In Fig. 4a the experimental DEPES data are presented at 1ML of Pt on Cu(111). In order to reveal the details of intensity patterns the background subtraction procedure was applied [24]. The distribution of the intensity maxima is similar to the DEPES results obtained for the clean Cu(111) surface (Fig. 3a). In MS calculations we considered different adsorption geometries and coexistence of adsorbate domains independently on their energetic justification. Therefore, in Fig. 4b–i the theoretical results obtained for 1ML of Pt on Cu(111) at A, B, on top (C), and bridge adsorption sites on Cu(111)