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Comment on "STM study of the (111) and (100) surfaces of PdAg, *Surf. Sci.* 417 (1998) 292–300" and references therein

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Highlights

- An error in the previously reported bulk composition of a PdAg(111) alloy is corrected.
- Bulk-sensitive energy-dispersive X-ray spectroscopy (EDS) was used to correctly determine the bulk composition of the material.

Abstract

Investigation of isolated, single atoms on the surfaces of alloys is of great interest in the field of heterogeneous catalysis. Prior studies by Nieuwenhuys, etal. [*Surf. Sci.* 417 (1998) 292–300 and references therein] showed that annealing the (111) surface of a PdAg bulk alloy yielded a surface with ~5% Pd, predominantly in the form of single atoms, rendering it an ideal model for investigating the reactivity of single Pd atoms. Herein, new evidence is reported that establishes the bulk composition of the PdAg(111) alloy studied previously is 67 % Ag and 33 % Pd, whereas it was reported to be 33 % Ag and 67 % Pd in the prior studies. Herein, the bulk composition of a crystal derived from the same PdAg alloy boule used previously was determined using energy-dispersive X-ray spectroscopy (EDS)—a bulk sensitive technique. Surface-sensitive measurements, including X-ray photoelectron spectroscopy, were also performed and are in good agreement with the prior studies by Nieuwenhuys, etal.

Keywords

Alloys; Palladium; Silver; Low-index single crystal surfaces; bulk composition

1. Introduction

Dilute alloys combine high reactivity of one component with selectivity derived by dilution within a second, less reactive metal. Recently, isolated, single atoms of reactive precious metals have been studied as a potential means of achieving optimal catalytic function [1]. To this end, a highly annealed PdAg alloy was shown to consist of mainly isolated Pd atoms on the (111) surface [2], making it an ideal model for investigating the reactivity of single Pd atoms.

Previously, a PdAg(111) bulk alloy crystal obtained from Metal Crystals Ltd., later acquired by Surface Preparation Laboratory, was used in multiple studies to investigate (1) the CO adsorption on the PdAg alloy surface [3], (2) the interaction of H_2 and CO on the PdAg alloy surface [4], (3) the surface composition and Pd distribution on a highly-annealed PdAg(111) alloy surface [2], and (4) oxygen adsorption [5]. In all cases, the authors cited the bulk composition of the alloy as 33 % Ag and 67 % Pd.

In the original work [2–5], no data were provided to determine the bulk composition of the alloy — only surface-sensitive methods were employed. Specifically, there were no data for a sputtered surface, which would expose the bulk composition; nor were there data for methods that probe bulk composition directly. The tools used to investigate the alloy in the original papers were Auger electron spectroscopy, low-energy electron diffraction and temperature-programmed desorption [3,4], followed by investigations using scanning tunneling microscopy (STM) [2,5]. All experiments were performed after annealing the clean surface to high temperature (820 K for 80 minutes) which changes the surface composition significantly in comparison to the bulk composition.

The surface exposed after high temperature annealing clearly had a deficit of Pd relative to the stated bulk composition. In the prior work, the Pd MNN / Ag MNN ratio in the Auger spectrum was measured to be 0.4 at a primary electron energy of 3 kV for a highly annealed surface [2], indicating that the material was ~35% Pd within the depth probed ($3\lambda = 95\%$), ~2.1 nm, based on the inelastic mean free path of the corresponding Auger electrons (333 eV kinetic energy) [7,8]. Given the estimated information depth of ~2.1 nm or about 9 atomic layers, these data suggest that the stated Pd concentration of 67% in the bulk was not correct. Subsequent studies performed on the same alloy crystal further indicated a very low concentration of Pd on the annealed surface of <10% and that the Pd atoms were mainly present as single, isolated atoms [2].

The predominance of Pd single atoms on the (111) surface observed using STM after heating the bulk PdAg alloy to high temperature is consistent with studies of thin-film PdAg (111) surface alloys created by depositing Ag (1ML) onto Pd(111) and subsequent annealing to 800 K. In the case of the thin film alloy, the silver remained on the surface after annealing despite the presence of bulk Pd(111) below. Furthermore, Pd monomers predominated on the surface alloy for compositions with more than 75% Ag [9].

Herein, new data are presented that probe the bulk and near surface region using energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) and demonstrate that the bulk composition is 67% Ag and 33% Pd. The data presented are for a crystal obtained from the same boule and same supplier as for the abovementioned prior work. The origin of the PdAg boule was confirmed with Surface Preparation Laboratory and Prof. Ludo Juurlink who stored the original alloy crystal at Leiden University following the retirement of Prof. Nieuwenhuys.

2. Experimental Methods

Energy-dispersive X-ray spectroscopy (EDS) was performed at 20 kV on JEOL JSM-7900F Field Emission Scanning Electron Microscope (FESEM) equipped with an Oxford Instruments UltimMax EDS detector. EDS data was quantified using AZtec ver. 5.1 software, which employs the XPP matrix correction protocol, and calibrated microanalysis standards. The sample was not thoroughly cleaned in vacuum prior to EDS; furthermore, it was exposed to air prior to analysis. Since EDS is sensitive to bulk composition, transport through air does not affect the measured Pd:Ag ratio.

X-ray photoelectron spectroscopy (XPS) was performed in an ultrahigh vacuum (UHV) system consisting of an analysis chamber (base pressure ~ 2×10^{-10} Torr) and a preparation chamber (base pressure ~4×10^{-10} Torr) described in detail elsewhere [10]. XPS measurements were conducted using non-monochromated Al Kα radiation (Perkin Elmer 04-548/32-095 with RBD 20-042). Photoelectrons were measured under emission angles of 0 degrees (normal) and 65 degrees (grazing) with respect to the sample normal using a hemispherical analyzer (SPECS Phoibos 100 equipped with a 5-channel electron multiplier). The inelastic mean free path is 1.6 nm for Ag 3d photoelectrons in Ag material, and 1.64 nm for Pd 3d photoelectrons in Ag material [11]. The XP data were corrected and quantified using Wagner's relative sensitivity factors [12]. The PdAg(111) sample (Surface Preparation Laboratory, previously Metal Crystals Ltd. located in Cambridge, UK) was extensively cleaned by repeated cycles of Ar^+ sputtering (15 min, 2 keV, 6 μA) and annealing in ultra-high vacuum (UHV) at 850 K (5 min) immediately before XPS measurements.

3. Results and Discussion

The bulk composition of the alloy crystal cut from the same rod as previous work by the Nieuwenhuys group [2–5] was measured to be approximately 34% Pd and 64% Ag using energy-dispersive X-ray spectroscopy (EDS) for the Pd and Ag Lα X-ray transitions (**Fig. 1**). Small concentrations (1-2%) of Si and Ni were also detected. The crystal was homogenous in composition, based on the uniform color map (**Fig. 1A**) and nearly identical quantitative analysis for the center and edge of the crystal (**Fig. 1B**). The sample hadn't been extensively cleaned before EDS measurements.

Analysis of X-ray photoelectron (XP) spectra of a sputtered surface to expose the bulk composition was consistent with the EDS data, indicating a bulk composition of 31% Pd and 69% Ag (**Fig. 2**). Impurities including Si and Ni could not be detected on the sputtered surface via X-ray photoelectron spectroscopy (XPS) after extensive cleaning of the bulk crystal. The information depth (3λ = 95%) of the XP experiments is ~4.8 nm or about 20 layers for measurements with normal emission angle and ~2.0 nm or about 8-9 layers for measurements with grazing emission angle.

The composition of the highly annealed surface was also analyzed using XPS (normal emission angle), yielding an average bulk composition of 26% Pd and 74% Ag (**Fig. 2B**). The drop in Pd content after annealing indicates that the Pd surface concentration is less than in the bulk material, consistent with <10% Pd observed in a prior STM study on a surface prepared under the same conditions [2]. A more pronounced drop in Pd $3d_{5/2}$ intensity from a sputtered to annealed surface by using a grazing angle in XPS (**Fig. 2A**) corroborates a lower Pd surface content after annealing due to the lower information depth for this angle-resolved XP measurement. The depletion of Pd in the surface layer upon annealing has also been observed previously on equilibrated Pd_xAg_{1-x}/Pd(111) surface alloy systems using STM and Monte Carlo simulations [9], and recently on annealed Pd/Ag(111) systems resulting in Ag-capped PdAg surface alloys using a combination of XPS, STM and density functional theory [10]. Further, grazing angle XP measurements lead to more pronounced XP core-level shifts (CLS), for instance, a CLS of about +0.2 eV after annealing (**Fig. 2A**), indicating a higher relative contribution of the silver-rich surface. The CLS are consistent with prior experimental [13–16] and theoretical [10,15] evidence on PdAg model systems. Narrower Pd $3d_{5/2}$ peaks after annealing, especially for the XP data acquired under grazing emission angle, indicates that the number of local environments of Pd has decreased; in agreement with the conclusion by the Nieuwenhuys group [2–4] that isolated Pd atoms predominate on the highly annealed surface.

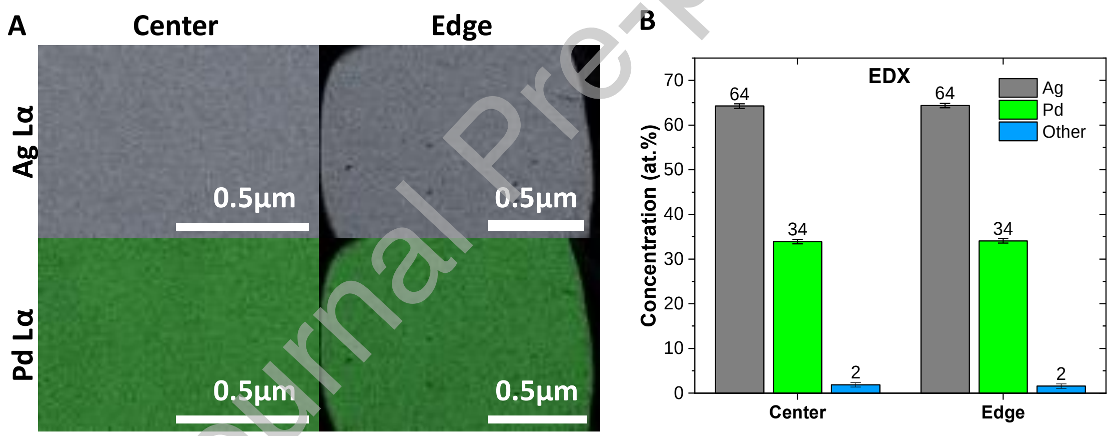

Fig. 1. The bulk composition of the PdAg(111) crystal corresponds to 34 % Pd and 64 % Ag as measured via energy-dispersive X-ray spectroscopy. The labels "Center" and "Edge" in (**A**) refer to the measured spot in the center and at the edge of the sample, respectively, and indicate a homogenous composition of the sample (**B**).

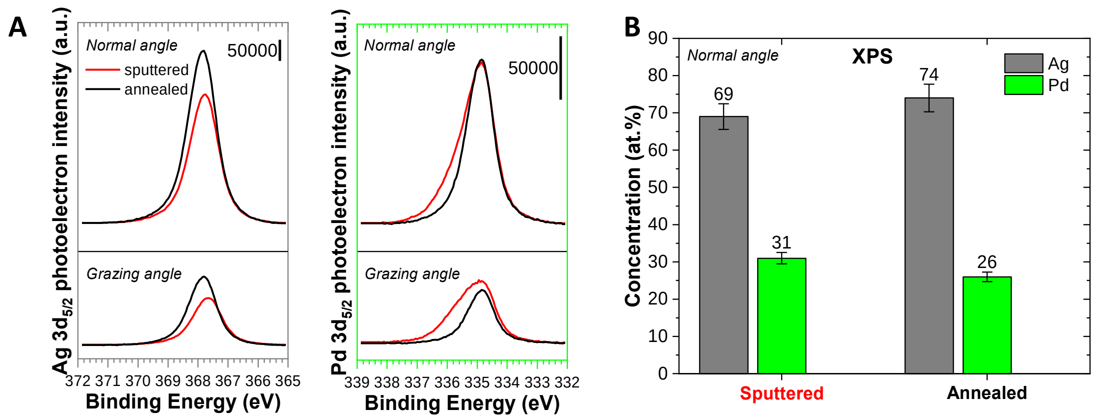

Fig. 2. The bulk composition of the PdAg(111) crystal corresponds to 31% Pd and 69% Ag using X-ray photoelectron spectra of a sputtered surface (red). The drop in Pd content to 26% after annealing (black) indicates that the surface concentration is less than in the bulk and is corroborated by grazing angle measurements which lower the information depth compared to measurements under normal angle. For measurements at grazing angle, 63% (1 λ) of the XP signal originates from the first 3 surface layers.

4. Summary

The bulk composition of a PdAg(111) alloy previously studied and reported to present a surface with predominantly Pd single atoms is 33% ± 1% Pd and 67% ± 2% Ag using a combination of EDS and XPS, showing that the composition was inadvertently transposed in the original papers.

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Author contributions

T.E. performed the XP experiments and data analysis, T.J.C. performed the EDS measurements and data analysis. The erratum was written by T.E. and C.M.F.

Competing Interests

The authors declare no competing interests.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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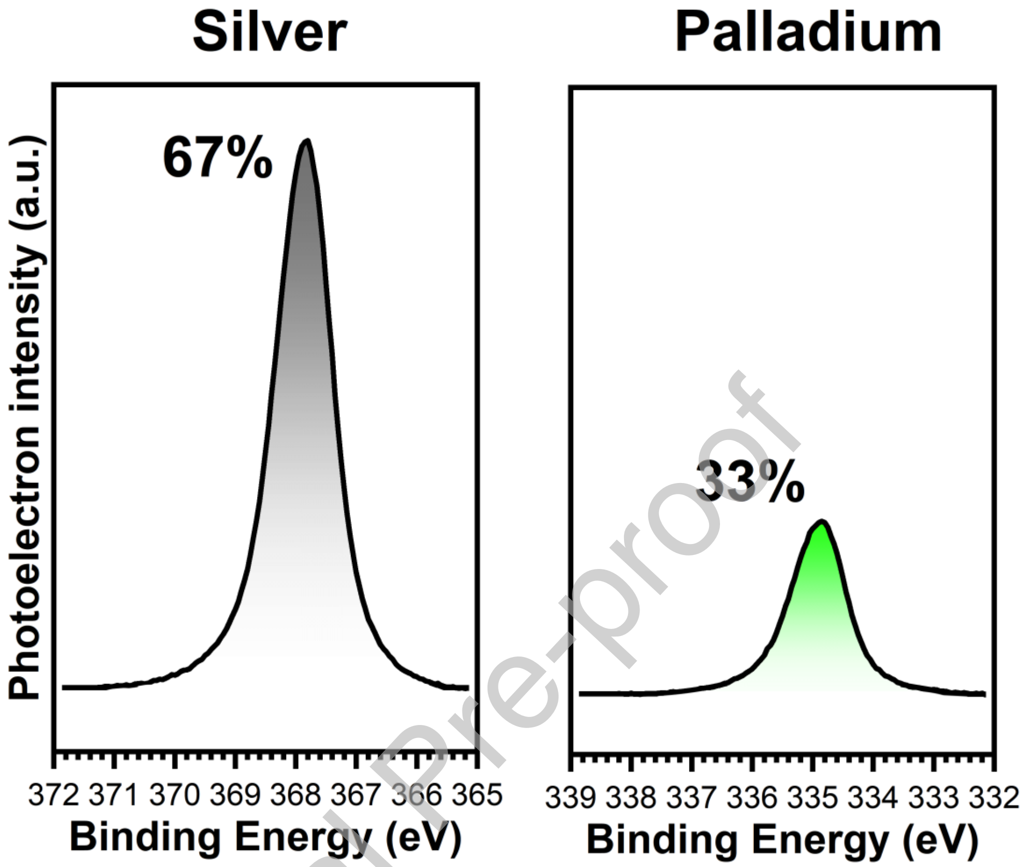
Silver
Palladium
67%
33%
Photoelectron intensity (a.u.)
372 371 370 369 368 367 366 365
339 338 337 336 335 334 333 332
Binding Energy (eV)
Binding Energy (eV)