Surface structure of Pd(111) with less than half a monolayer of Zn†

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We have characterized the structural properties of submonolayer amounts of Zn on Pd(111) using scanning tunneling microscopy (STM) and spot-profile analysis low energy electron diffraction (SPA-LEED). Following room temperature deposition of \( \approx 0.06 \) monolayers (ML) Zn onto Pd(111), we observe the substitution of Zn for Pd in the surface layer. At \( \approx 0.20 \) ML of deposited Zn, STM reveals a locally ordered phase with a \( (2\sqrt{3} \times 2\sqrt{3})R30^\circ \) unit cell located near Zn substitutions; SPA-LEED patterns reveal the same periodicity. We attribute this phase to the metastable bonding of atoms or clusters predominantly in hollow sites surrounding Zn substitutions in the surface layer. At \( \approx 0.4 \) ML, STM images reveal local \( (\sqrt{3} \times \sqrt{3})R30^\circ \) and \( (2 \times 1) \) ordering on surfaces annealed to 350 K. At coverages near 0.5 ML, both STM and SPA-LEED show the onset of the formation of the \( (2 \times 1) \) ordering associated with the Zn:Pd 1:1 alloy phase. At all coverages, the surface is dominated by island growth; the islands’ size and density is shown to depend critically on annealing at temperatures as low as 350 K. These results provide insight into the structural features of a Zn/Pd(111) coverage regime that has been much debated in recent years.

Introduction

Near-surface alloys (NSAs) are appealing candidates for applications in heterogeneous catalysis. Control of the composition or geometry of an alloy can allow for the manipulation of critical physical and electronic properties, leading to tailored selectivity and enhanced chemical reactivity. In particular, the catalysis of the steam reforming of methanol (\( \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2 \)) is of considerable current interest, largely because of its relevance to hydrogen fuel cells. Several NSAs have been proposed as catalysts selective for this reaction. However, since elemental Cu lacks the critical component of the Pd/ZnO system which is highly active for steam reforming reactions, including Au/Ni and Pt/Ni for methanol steam reforming, and Zn/Pd which is hypothesized to be the critical component of the Pd/ZnO system which is highly active for methanol steam reforming (MSR). The ZnPd 1:1 alloy phase has a d-band structure that is remarkably similar to that of Cu, which is widely-used in MSR, as it is both active and selective for this reaction. However, since elemental Cu lacks long-term stability, largely due to the effect of sintering at process temperatures, the pursuit of a suitable alternative continues, mandating the need for a better understanding of other candidate catalysts.

Previous structural characterizations of the Pd/Zn NSA have focused largely on this 1:1 alloy phase, which can be formed by depositing Zn on Pd(111) either deposited directly onto a surface held at \( >450 \) K, or post-annealed at the same temperature. It has also been formed at room temperature on successively deposited bilayers at \( >1 \) ML Zn (either deposited directly onto a surface held at \( >450 \) K, or post-annealed at the same temperature). It has also been formed at room temperature at a Zn coverage of \(~0.5\) ML, although in this case the authors also suggest that it grows in bilayer patches. For alloys formed in the former manner, the atomic rows are corrugated such that the Zn sits slightly above the Pd, but this corrugation can be reversed by higher-temperature annealing, which reduces the amount of Zn in the subsurface layers. In contrast to the extensive work on the 1:1 NSA, few structural characterizations exist of Pd(111) surfaces with low (<0.5 ML) coverages of Zn. Based on LEED, Jeroro et al. propose that a p\((2 \times 2)\) phase is formed when 0.25 ML Zn is annealed to 550 K. However, since the LEED pattern for a p\((2 \times 2)\) structure is qualitatively indistinguishable from the pattern of a three-domain p\((2 \times 1)\) reconstruction, the interpretation of the p\((2 \times 2)\) phase is not unequivocal.
Temperature-programmed desorption (TPD) results suggest that a thorough understanding of Zn-poor surfaces could be relevant to the optimization of MSR over Zn/Pd, since very low Zn coverages (0.03–0.06 ML) on Pd(111) are associated with a high-temperature (360 K) desorption peak for formaldehyde (CH$_2$O), a reaction intermediate for MSR.$^{23}$) Furthermore, previous studies have failed to correlate the extent of the alloy formation with either the selectivity$^{24}$ or the activity$^{25}$ of ZnO-supported Pd catalysts; however, those studies contradict the majority of work on the topic, which suggests that the 1:1 alloy phase is selective and active for MSR.$^{26}$) and have even revealed details of the dependence of catalytic selectivity on the subsurface composition.$^{29}$) Regardless, since the nature of the low-coverage Zn/Pd(111) system is not yet understood, it remains an active topic in the literature. Monte Carlo simulations of the behavior of submonolayer Zn on Pd(111) show that Zn preferentially exchanges with Pd in the substrate layer, creating a Pd-rich adlayer covered with small (3–5 member) Pd clusters.$^{27}$) *Ab initio* calculations indicate that a number of different small (2–5 member) clusters, considered for various cluster and surface Zn:Pd stoichiometries, produce a CH$_2$O binding energy of about 1 eV, which, according to Redhead analysis, should correspond to a 360 K desorption peak.$^{28}$

Here we report a combined scanning tunneling microscopy (STM) and spot profile analysis (SPA)-LEED study performed to elucidate the behavior of small quantities (<0.5 ML) of Zn on Pd(111). As opposed to conventional LEED, which has previously failed to reveal any organized structure at Zn coverages below 0.25 ML$^{22,23}$) both of these complimentary techniques are highly sensitive — SPA-LEED due to its high dynamic range and large transfer width,$^{29}$) and STM due to its ability to detect local ordering at surfaces.$^{30}$) Using this approach, we were able to elucidate the surface structure of very low coverage Zn/Pd(111) surfaces, including the identification of two previously unreported locally-ordered phases: one that appears to involve the stabilization of adatoms or clusters near Zn substitutions in the Pd(111) surface layer, and a $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase that occurs near $\approx 0.4$ ML Zn.

**Experimental**

Clean Pd(111) surfaces were prepared by repeated cycles of temperature ramping during oxygen exposure (up to 800 K at $2 \times 10^{-7}$ mbar), ion sputtering (1.5 kV Ar$^+$) and annealing (1000 K). Surface quality was confirmed by SPA-LEED or STM prior to deposition of Zn. Zn was deposited from a commercial Knudsen cell evaporator (CreaTec Fischer & Co. GmbH) fitted with a home-built shroud similar to the one described in ref. 31. The evaporator temperature was held near 375 K for all depositions. Following depositions of more than $\approx 0.25$ ML Zn, surfaces studied by STM were annealed for 5 minutes at 350 K to facilitate imaging (see later). STM measurements were made at INRS-ÉMT in Varennes, QC, Canada, with a commercial instrument (Aarhus 150, SPECS Surface Nano Analysis GmbH). Bias voltages were applied to the sample with respect to the tip. Images were processed with the WSxM software,$^{32}$ which was used to filter the images and correct them to the known Pd(111) lattice. SPA-LEED was performed in a separate chamber at the Surface Science Laboratory of Elettra-Sincrotrone Trieste using a commercial SPA-LEED (Omicron NanoTechnology GmbH) controlled with locally developed software.

The Zn coverage was calibrated using a quartz crystal microbalance (QCM) in STM experiments, and *via* examination of the intensity oscillation of the zero-order diffraction beam with coverage in the SPA-LEED experiments. As has been previously noted,$^{33}$) precise determination of Zn coverage is nontrivial. Indirect calibration based on rate estimation is made difficult due to coverage-dependent changes in the sticking probability. Accurate estimation of monolayer formation in SPA-LEED requires *a priori* knowledge of the growth mechanism including a detailed understanding of the subsurface interdiffusion of Zn. Moreover, the same considerations affect the interpretation of peak intensity in X-ray photoelectron spectroscopy (XPS), where inelastic mean free path analyses are often used to estimate overlayer thickness. As we discuss later, the energetics dictating Zn distribution in the top layers appear to be quite subtle near room temperature. Despite these challenges, we estimate that our coverages in both STM and SPA-LEED are accurate to within 20%, and note that both experimental methods show the onset of the $p(2 \times 1)$ phase at $\approx 0.5$ ML Zn, consistent with previous work.$^{18}$

**Results**

Fig. 1a shows an STM image of both a surface deposited with $\approx 0.06$ ML of Zn at room temperature (RT). The hexagonal arrangement of the $(1 \times 1)$ lattice is clear, with the large majority of the atoms exhibiting identical contrast. A minority of sites appear very dark; we interpret these as Zn substitutions (see Discussion) and will henceforth refer to these dark atoms as Zn. The line profile shown in Fig. 1b demonstrates the difference in contrast between the two atom types, and as well as the bright appearance of the atoms immediately surrounding the Zn substitutions. Subsurface sulphur impurities like the one indicated by the white dashed triangle in Fig. 1 were occasionally observed on both clean and Zn-exposed surfaces.$^{34}$) The surface appears qualitatively similar at both positive and negative scan biases (see ESI).

The morphology of surfaces deposited with $\approx 0.2$ ML of Zn shows a distinct dependence on the tunneling conditions. Fig. 2a and b show two STM images taken sequentially, under slightly different bias conditions, in the same area. The appearance of the surface in Fig. 2a is qualitatively similar to that in Fig. 1. Zn substitutions surrounded by brighter atoms are the dominant features; the overlaid lattice clearly shows that both of these features lie on Pd(111) top sites, and the inset 2D-fast Fourier transform (FFT) indicates the predominance of this periodicity. At slightly higher bias voltage (508 mV as compared to 450 mV), new features dominate the image. Fig. 2b shows a structure with a periodicity different from that of the substrate surrounding the black Zn substitution sites. The overlaid $(1 \times 1)$ lattice shows that the bright features of this new phase lie predominantly on hollow sites, although some occupy bridge sites. The inset FFT reveals
diffuse spots corresponding to a larger lattice rotated by 30° with respect to the (1 × 1). The local ordering surrounding the Zn substitutions is evident over a range of bias voltages, including some that allow the simultaneous imaging of this new phase and the surrounding (1 × 1) phase, as shown in Fig. 2c. This image clearly shows that the hollow-site phase is localized near Zn substitutions, and does not extend across the whole surface. The inset FFT contains contributions from both surface phases.

To confirm the presence of this phase, we collected SPA-LEED patterns following the same preparation procedures. In addition to a contribution from the (1 × 1) lattice (bright outer spots), SPA-LEED reveals a diffuse \((2/\sqrt{3} \times 2/\sqrt{3})R30^\circ\) pattern (hereafter \(2/\sqrt{3}\)), with new broad spots indicated in Fig. 2d by white arrows. We attribute these features to the poorly organized structure shown in Fig. 2b. These spots persist up to a coverage of \(\approx 0.25\) ML. Above this coverage the \(2/\sqrt{3}\) pattern is extinguished. The spot profiles permit estimation of the size of the domains contributing to these diffraction peaks, via the relation \(\Delta k/k = a/D\), where \(\Delta k\) is the full-width at half-maximum (FWHM) of the spot, \(k\) is the magnitude of the reciprocal lattice vector, \(a\) is the lattice constant, and \(D\) is the domain size. Based on an azimuthal measurement, the magnitude of \(D\) estimated for the \(2/\sqrt{3}\) phase present in the diffraction pattern in Fig. 2d is approximately 10 Å, which is in reasonable agreement with the domain sizes observed by STM.

STM imaging was difficult on as-deposited surfaces in the coverage range from \(\approx 0.25\) ML to \(\approx 0.50\) ML. A high density of islands dominates the images (see below), and noise along the fast-scan direction, consistent with diffusing species on the surface, precluded the observation of surface-layer structures. STM image quality was noticeably improved following a brief (5 minute) anneal to 350 K. Fig. 3a and b show typical STM images obtained on surfaces deposited with \(\approx 0.30\) ML of Zn and subsequently annealed. In contrast with the unannealed surfaces, we do not observe the local \(2/\sqrt{3}\) phase around the substitutions on annealed surfaces. Instead, we observe a wide range of atomic contrasts within the (1 × 1)-arranged surface atoms, which persist across a range of bias voltages. At \(\approx 0.4\) ML Zn, the surface contains a large number of Zn substitutions that exhibit short-range order which is predominantly \((\sqrt{3} \times \sqrt{3})R30^\circ\) but also includes small regions of \(p(2 \times 1)\), as shown in Fig. 3c. This \((\sqrt{3} \times \sqrt{3})R30^\circ\) ordering was not observed in SPA-LEED.
Larger area images show that second layer (island) growth is present following any amount of Zn deposition. The number density and size of islands increases with coverage. Annealing produces marked changes in the shape and density of islands on the surface. Fig. 4 shows a surface with \( 0.40 \) ML Zn before and after annealing to 350 K for 10 minutes. The most significant change is in island ripening: annealing produces larger, more compact structures, although some small compact islands also remain in regions away from the larger ones. The measured island height is \( \approx 2 \) Å, in agreement with the expected step height on Pd(111). On both the annealed and as-deposited surfaces, we observed small regions of third-layer growth on top of larger islands. Atomic resolution images obtained from islands show that they have a structure that is qualitatively identical to the substrate layer (see ESI\(^\dagger\)).

At coverages near 0.5 ML, STM images reveal a high surface density of the \( p(2 \times 1) \) phase, as shown in Fig. 5a. Although the real-space appearance of the structure is quite defective, the FFT (inset) clearly demonstrates the periodicity. The \( p(2 \times 1) \) phase grows directly in the substrate surface layer, not only on islands as has previously been observed.\(^{18}\) Around the same coverage, SPA-LEED reveals the emergence of a three-domain \( p(2 \times 1) \) pattern, shown in Fig. 5b. This pattern intensifies with increasing Zn deposition. STM images also show a better-defined surface structure with increasing Zn coverage; at \( \approx 1.8 \) ML (Fig. 5c) the \( p(2 \times 1) \) phase is extremely well developed, and contains bright defects distributed along its rows.

**Discussion**

Consistent with the Monte-Carlo-based prediction that Zn will exchange with substrate Pd,\(^{27}\) we propose that the dark features that appear in STM images following \( \approx 0.06 \) ML Zn deposition (cf. Fig. 1) are Zn substitutions in the Pd(111) surface layer. The substitution of Au in the Ni(111) surface produces qualitatively similar STM images, including the bright appearance of atoms surrounding the substitutions, which in the case of Au/Ni(111) the authors attribute to a combination of geometric and electronic effects;\(^{8}\) we attribute the enhanced contrast for atoms neighboring Zn substitutions in Pd(111) to similar phenomena. STM images of the low-coverage regimes of both Ag/Pd(111)\(^{35}\) and V/Pd(111)\(^{36}\) are also qualitatively very similar to our images of Zn/Pd(111). In the case of V/Pd(111), LEIS measurements confirmed that the V was confined to the topmost surface layer.\(^{36}\) Furthermore, STM data from the Zn/Pd(111) \( p(2 \times 1) \) phase also indicate that the Zn atoms image with very low contrast over a range of bias voltages.\(^{17}\) In our experiments, the number of black features scales with the amount of deposited Zn, as expected. Contrary to expectation, we frequently observed nearest-neighbor Zn atoms, even though DFT predicts that Zn–Zn bonds are energetically unfavorable with respect to Zn–Pd bonds.\(^{17}\) The emergence of \( (\sqrt{3} \times \sqrt{3}) \) \( R30^\circ \) ordering following annealing at 350 K is interesting in this light, since this phase (which corresponds nominally to 0.33 ML coverage) maximizes Zn–Pd bonds. This could indicate that the energy barrier for Zn–Pd exchange for a Zn atom with a one Zn–Zn bond is not easily overcome at room temperature, but is surmountable at 350 K.

Fig. 4  Island structure on an as-deposited surface with \( \approx 0.40 \) ML Zn (a), and after annealing to 350 K (b). STM image parameters: \( V_b = -44 \) mV (a) and 251 mV (b). The scale bar in each image is 7.5 nm.

**Fig. 3**  (a) and (b) Variable contrast of the substrate atoms on a surface with \( 0.30 \) ML Zn after annealing to 350 K. The black contrast of the Zn substitutions is evident at both positive and negative bias voltages, as are the range of contrasts in the surrounding substrate layer. STM image parameters: \( V_b = 60 \) mV (a), \( V_b = -72 \) mV (b). (c) Local ordering of Zn substitutions in a surface deposited with \( \approx 0.40 \) ML Zn and annealed at 350 K. Regions of both \( (\sqrt{3} \times \sqrt{3}) \) \( R30^\circ \) and \( p(2 \times 1) \) ordering are evident on the surface. The inset FFT contains contributions from both the \( 1 \times 1 \) lattice and the \( (\sqrt{3} \times \sqrt{3}) \) \( R30^\circ \) regions. STM image parameters: \( V_b = 12 \) mV. The scale bar is 1 nm.
feature can the CH$_2$O desorption peak at 360 K be attributed – are there clusters on the surface? (2) can the $p(2 \times 2)$ phase at 0.25 ML be confirmed? Our results address both of these questions.

Through their Monte Carlo simulations and ab initio calculations, Chen and coworkers established that small clusters should be present on the low coverage Zn/Pd(111) surface, and that some of these clusters may present CH$_2$O bonding sites that are consistent with the observed 360 K TPD peak. At coverages around 0.2 ML, our STM images indicate the presence of a locally ordered phase surrounding Zn substitutions. SPA-LEED confirms that the periodicity matches that expected for the trapping of adsorbates in hollow sites, as shown in Fig. 6. Since Pd is liberated by Zn exchange, we propose that the adsorbates, either clusters or adatoms, are predominantly composed of Pd, however some presence of Zn can also be expected. These adsorbates are only metastably bound as they appear indistinct both in STM images, where they image as large protrusions without clear definition, and in SPA-LEED, where the corresponding diffraction spots are diffuse. Though their appearance and disappearance with changing bias voltage in STM images (Fig. 2) suggests an electronic effect, we could not pinpoint any bias voltages that consistently revealed or suppressed these features. Therefore, their presence or absence in STM images likely originates from interaction of the surface with the tip, i.e. the tip ‘sweeping away’ the adsorbates when it is brought close to the sample. We observed this phase at $\approx 0.20$ ML Zn in both STM and SPA-LEED, but did not directly observe it at the lower coverages (0.06 ML) implied by the CH$_2$O TPD results. The very low bias voltages that produced favourable imaging on the 0.06 ML surfaces may have precluded our observation of this phase, since the tip is very close to the surface under these conditions. On the other hand, it is possible that the formation of the phase requires a critical density of diffusing species that is not attained at low Zn coverages.

Additional evidence for the presence of weakly bound species on the surface arises from the difficulty in STM imaging without annealing the surface at coverages over $\approx 0.25$ ML. The noisy, streaky imaging conditions of unannealed surfaces in this coverage range are consistent with the presence of weakly bound species on the surface. The loss of $2/\sqrt{3}$ order in SPA-LEED in this coverage range further indicates a fundamental change in the surface between the low-coverage quasi-ordered phase and this regime. Since SPA-LEED shows no superstructure, and STM imaging was not successful, we cannot comment on the atomic ordering of the unannealed surface between 0.25 and 0.5 ML Zn.

The annealed surface, however, was easily imaged by STM, and exhibits two distinguishing features. First, the substrate atoms between the Zn substitutions manifest a range of contrasts (cf. Fig. 3a and b), rather than the consistent contrast observed without annealing (cf. Fig. 1). We attribute this effect to the diffusion of Zn into the subsurface layers. A similar effect was observed for V/Pd(111) with high temperature treatment. Second, Zn substitutions were observed to locally order, forming regions of $(\sqrt{3} \times \sqrt{3})$R30° and $p(2 \times 1)$ (cf. Fig. 3c); we note that these two phases share a common periodicity along the $\{112\}$ lattice directions, and therefore that the $(\sqrt{3} \times \sqrt{3})$R30° is a logical precursor to the $p(2 \times 1)$, which occurs at a higher Zn : Pd stoichiometry (1 : 1 vs. 1 : 2).

This first observation, combined with the change in island shape, size and density (cf. Fig. 4), suggests that annealing

![Fig. 6](image_url) Geometry of the hollow-site phase. Pd atoms are shown in gray, and a Zn substitution is shown as a dark purple atom. The red dots indicate the hollow sites that are metastably occupied by atoms or clusters.
disfavors the presence of small islands and clusters on the surface, and promotes the incorporation of the diffusing species into either the surface or adlayer, with some amount of Zn diffusing deeper into the substrate. The change in surface chemistry and structure resulting from a relatively modest energy input (350 K) is staggering, and suggests that the energetics of this system are extremely variable in a temperature window around room temperature.

Hence, we can address the two outstanding questions as follows: (1) our data are consistent with the presence of clusters on Zn/Pd(111) surfaces at coverages near 0.20 ML and above, and (2) we failed to find evidence of a $p(2 \times 2)$ phase at 0.25 ML with either STM or SPA-LEED.

**Conclusions**

A combined STM and SPA-LEED investigation has elucidated the morphologies associated with $<0.5$ ML Zn on Pd(111). Starting at very low coverage ($\approx 0.06$ ML), STM reveals the substitution of Zn atoms into the Pd(111) surface. At coverages near $\approx 0.20$ ML, both STM and SPA-LEED indicate a local $(\sqrt{3} \times \sqrt{3})R30^\circ$ ordering of adsorbates on hollow sites near Zn substitutions. Increasing Zn coverage above $\approx 0.25$ ML extinguishes the $2/\sqrt{3}$ symmetry in SPA-LEED and leads to deterioration of STM images, consistent with a large density of diffusing species on the surface. Following annealing to 350 K, STM reveals that surfaces with $\approx 0.25$ ML to $\approx 0.40$ ML of Zn exhibit local ordering of the Zn substitutions, including the formation of patches of $(\sqrt{3} \times \sqrt{3})R30^\circ$ and $p(2 \times 1)$ reconstructions. Finally, near 0.5 ML, both STM (annealed) and SPA-LEED (annealed) surfaces indicate the formation of larger domains of $p(2 \times 1)$, consistent with the 1:1 Zn : Pd alloy. Both the STM and SPA-LEED indicate an increased quality of the reconstruction with increased Zn coverage above 0.5 ML.

These results corroborate recent theory results regarding the presence of clusters on the Zn/Pd(111) surface, and provide new insight into the incorporation of small amounts of Zn into the surface, in particular demonstrating both the subtlety of the energetics and the need for local probe methods to reveal local ordering.

**Acknowledgements**

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) through the Discovery Grants program and in the form of a Postdoctoral Fellowship (JMM), by Le Fonds de recherche du Québec – Nature et technologies (FRQNT), and by the Ministère du Développement Économique, Innovation et Exportation (MDEIE). The authors thank Dr Markus Kratzer for his advice regarding the construction of the Zn evaporator.

**Notes and references**