Alloy Formation and Chemisorption at Zn/Pt(111) Bimetallic Surfaces Using Alkali ISS, XPD, and TPD

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ABSTRACT: Alloy formation and chemisorption at bimetallic surfaces formed by vapor-depositing Zn on a Pt(111) single crystal were investigated primarily by using X-ray photoelectron diffraction (XPD), X-ray photoelectron spectroscopy (XPS), low-energy alkali ion scattering spectroscopy (ALISS), low electron energy diffraction (LEED), and temperature programmed desorption (TPD). A wide range of conditions were investigated to explore whether deposition and annealing of Zn films could produce well-defined, ordered alloy surfaces, similar to those encountered for Sn/Pt(111) surface alloys. These attempts were unsuccessful, although weak, diffuse (2 × 2) spots were observed under special conditions. The particular PtZn bimetallic alloy created by annealing one monolayer of Zn on Pt(111) at 600 K, which has a Zn composition in the surface layer of about 5 at. %, was investigated in detail by using XPD and ALISS. Only a diffuse (1 × 1) pattern was observed from this surface by LEED, suggesting that no long-range, ordered alloy structure was formed. Zn atoms were substitutionally incorporated into the Pt(111) crystal to form a near-surface alloy in which Zn atoms were found to reside primarily in the topmost and second layers. The alloyed Zn atoms in the topmost layer are coplanar with the Pt atoms in the surface layer, without any “buckling” of Zn, that is, displacement in the vertical direction. This result is expected because of the similar size of Pt and Zn, based on previous studies of bimetallic Pt alloys. Zn atoms desorb upon heating rather than diffusing deep into the bulk of the Pt crystal. Temperature programmed desorption (TPD) measurements show that both CO and NO have lower desorption energies on the PtZn alloy surface compared to those on the clean Pt(111) surface.

1. INTRODUCTION

Pt is one of the most widely used catalytic metals in the chemical and petroleum industries.1,2 In nearly all, if not all, of these applications, Pt-based heterogeneous catalysts usually incorporate additional metal components to improve performance.3,4 Moreover, Pt alloy surfaces can be formed through interactions with supporting substrates. For example, it is well established that platinum supported on substrates such as zinc aluminate (ZnAl2O4) will result in the formation of Pt−Zn alloys by reducing ZnO impurities thus altering the characteristics of the catalyst performance.4,5 Thus, it is of interest to explain the origin of the changes in Pt-based catalyst performance due to a second metal, and specifically the presence of Zn. These surfaces are known to have altered structural, chemical, electronic, and catalytic properties compared to those of the single-component substrates.3,5,6−11 Rodriguez et al. previously studied the chemical properties and electronic structure of various Pt−Zn surfaces,12,13 but no other more extensive studies exist. In particular, more information on the Pt−Zn alloy structure is needed, especially seeking ordered alloy phases that may be formed. For example, in related studies, it was shown by Bayer et al.14 and Jeroro et al.15 that Zn deposited on Pd(111) surfaces and then subsequently annealed to 550 K produced a well ordered p(2 × 1)-Zn/Pd(111) surface alloy. The current paper reports on our characterization of the atomic structure of Pt−Zn bimetallic alloy surfaces, similar to our previous work on Pt−Sn surface alloys,16,17 our attempts to discover conditions to produce ordered Pt−Zn surface alloys and provide further insight into the chemical properties of Pt−Zn alloy surfaces.

Previous work in our groups has focused on the synthesis and characterization of ordered, bimetallic surfaces prepared by vapor deposition of a second metal component on a transition metal substrate. For example, we have prepared several ordered alloy, or intermetallic compound, surfaces involving Pt−Sn,16,18 Pd−Zn,15,19 Pd−Cu,20 Rh−Sn,21 Ni−Sn,22 and Pt−Ge.23

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systems. Such ordered bimetallic surface alloys are helpful in clarifying the origins of the changes that occur in the chemistry of the substrate metal due to either geometric and electronic effects because of the well-defined composition and structure of these surfaces.

While there are several ordered surface alloys that can be prepared by vapor deposition of Sn on Pt, that is, the \((2 \times 2)\)-Sn/Pt(111), \((\sqrt{3} \times \sqrt{3})R30^\circ\)-Sn/Pt(111), \(c(2 \times 2)\)-Sn/Pt(100), and \((3 \times 2)\)-R45^\circ\)-Sn/Pt(100) structures, there are not many other closely related systems available. The other UHV chamber that was used in this study was equipped with a Stanford Research Systems (SRS) QMS for TPD analysis and a quartz crystal film thickness monitor (Qpod, Inicon) for measuring Zn deposition rates. This system also had a hemispherical electron energy analyzer and dual Al/Mg K\( \alpha \) X-ray source for XPS.

The Pt(111) single crystal substrates used in this study were ~10-mm diameter \(x\) 1.0-mm thick, and oriented to within \(\pm 0.5^\circ\). The sample azimuthal orientation was identified coarsely by LEED alignment and then finely by XPD polar and azimuthal scans. The crystals were mounted onto the sample manipulator by two 0.015" W wires either spot-welded to or clamped in two slots on the sample edges. Temperature was monitored by a chromel-alumel thermocouple spot-welded to the edge of the crystal. The crystal was cleaned by repeated cycles of Ar\(^+\) ion sputtering and oxygen treatment (5 \(\times\) \(10^{-8}\) Torr \(O_2\), 850 K, 5 min) to remove segregated surface carbon and subsequent annealing in vacuum at 1200 K to desorb residual oxygen. Surface cleanliness and ordering was verified by XPS and a sharp \((1 \times 1)\) LEED pattern, respectively.

Zn was deposited using evaporative Zn sources consisting of a piece of high-purity Zn wire (ESPI, 5 N, 0.010 in. diameter) wrapped around a 0.020 in. diameter W filament. To deposit Zn atoms onto the Pt(111) surface, the temperature of the Zn doser was raised until deposition was observed. The doser temperature was monitored by a chromel-alumel thermocouple spot-welded to the W filament of the doser, and the doser was typically operated at 500 K. The Zn coverage is reported as effective monolayers where one monolayer was assumed to be \(1.5 \times 10^{15}\) atom/cm\(^2\), which is the density of Pt atoms on the Pt(111) surface.

The XPD results presented here use a polar angle \(\psi\) that is defined with respect to the surface normal, with \(\psi = 0^\circ\) corresponding to positioning the analyzer perpendicular to the surface plane. The angle between the analyzer and the X-ray source was fixed at 42.5°. Mg K\( \alpha \) X-rays were used for both XPS and XPD. The X-ray source was operated at 300 W (15 kV) and a pass energy of 93.9 eV was used on the SCA for both XPS and XPD. Spectra for the Pt 4f and Zn 2p\(3/2\) core-level peaks were obtained with a 0.2-eV step size, and the Pt and Zn intensities used in XPD were measured from peak areas after background subtraction. In XPD, a data point (energy scans for both Pt and Zn) was acquired every 17.5 s and a complete angular line scan was obtained in about 20 min.

Na\(^+\) alkali ions were produced from a solid state source mounted in the ionizer region of the Colutron ion gun. Na\(^+\) ions were thermally emitted from a cartridge containing an aluminosilicate charge which has been loaded previously with sodium ions by ion-exchange. This type of ion emitter is very durable, and does not react with the ambient atmosphere during storage. In these ALISS measurements, a Na\(^+\) beam energy of 1.0 keV was used at a current density of 45 pA/mm\(^2\) at the Pt(111) sample. The SCA was operated at a pass energy of 1127.1 eV for ALISS, and a complete energy scan could be acquired every 1 min, with a 1-eV step size. A complete polar angle scan could be obtained in 90 min. The angle between the analyzer and ion source was fixed at 36° to give a scattering angle of 144°. Conventionally in ALISS, the polar angle \(\Psi\) is defined with respect to the crystal surface, with \(\Psi = 90^\circ\) corresponding to ions incident perpendicular to the surface. ALISS polar scans were obtained for \(\Psi = 0^\circ - 90^\circ\). An energy scan was obtained at every polar angle from \(E_\psi/E_\theta = 0.1 - 0.7\), which fully covers the scattering peaks from Pt and Zn.

2. EXPERIMENTAL METHODS

The experiments were performed in several different UHV surface analysis chambers. The primary two-level UHV chamber that was used for the LEIS experiments has been described in detail elsewhere. The base pressure of this chamber has been \(1 \times 10^{-10}\) Torr. The upper level contained a four-grid LEED optics and UTI 100C quadrupole mass spectrometer (QMS) for temperature programmed desorption (TPD). The lower level was equipped with a Colutron ion gun providing collimated and monoenergetic ion sources for LEIS, dual-anode Al/Mg K\( \alpha \) X-ray source for XPS and XPD, Perkin-Elmer Model 10–360 spherical capacitor analyzer (SCA) with a multichannel detector at a fixed scattering angle \(\theta\) of 144°, electron gun for AES, and ion sputtering gun. Gas and metal dosers were located at convenient positions throughout the chamber on both levels.

The sample manipulator rotated in polar (\(\pm 180^\circ\)) and azimuthal (\(\pm 90^\circ\)) planes. Both rotations were controlled by stepping motors operated either manually or interfaced through a computer. The accuracy of the polar angle (\(\psi\) for XPD and \(\Psi\) for ALISS), azimuthal angle \(\phi\), and scattering angle \(\theta\) were \(\pm 0.5\), \(\pm 1\), and \(\pm 0.5^\circ\), respectively.
scattering signal intensity could be easily taken from the Pt peak height, and this gave the same result as measuring the Pt peak area. Because of the low intensity and high background, the Zn scattering signal intensity was calculated from the Zn peak area after background subtraction.

3. RESULTS AND DISCUSSION

3.1. Preparation of PtZn Alloy. XPS and TPD were initially used to characterize the growth and thermal evolution of vapor-deposited Zn layers on the Pt(111) surface. Figure 1 shows the position of the Zn(2p 1/2) XPS peak as a function of annealing temperature for a 0.2 ML Zn film on Pt(111). Between 300 and 450 K, the Zn(2p 1/2) binding energy is 1044.77 eV, which is consistent with that reported previously for Zn adatoms on the Pt(111) surface.12,34 Annealing the 0.2 ML Zn/Pt(111) sample to temperatures above 500 K caused an ∼0.5 eV decrease in the Zn(2p 1/2) binding energy indicating a change in the chemical environment of the Zn atoms. This result is in agreement with the previous study of Rodriguez et al.12,13,35 in which it was concluded that adsorbed Zn atoms become incorporated into the Pt(111) surface to form a PtZn alloy upon heating above 400 K.

Figure 2 shows Zn TPD spectra obtained from Zn-dosed Pt(111). Spectrum A corresponds to a sample that was dosed with 1 ML of Zn (as determined by the film thickness monitor) at 300 K, followed by annealing at 600 K for 2 min. This spectrum contains a Zn desorption peak at 840 K. As shown in Figure 3, the area of this peak increased linearly with Zn coverage up to 1 ML at which point it became saturated with the area remaining constant at higher coverages. Curve B in Figure 2 corresponds to a Zn desorption spectrum obtained from a Pt(111) sample dosed with 2 ML of Zn at 300 K. For this coverage, in addition to the peak at 840 K, a narrower peak of similar area is also present at 550 K. The area of the lower-temperature peak was found to increase linearly with Zn coverage for coverages greater than 1 ML. Based on the XPS and TPD results, the high-temperature Zn desorption peak can be assigned to Zn atoms that have reacted with the Pt(111) surface to form an alloy, while the low-temperature peak can be assigned to Zn atoms adsorbed on the PtZn alloy surface.

TPD experiments were also performed with samples for which 1 ML of Zn was deposited and annealed at 600 K to form the alloy, followed by deposition of a second Zn monolayer at 300 K. The TPD spectra obtained from these samples were identical to curve B in Figure 2. These results demonstrate that for the various sample preparation methods used in this study, the amount of Zn that can be incorporated into the Pt(111) surface is limited to 1 ML. Figure 4 depicts the schematic of different preparation methods for Zn/Pt(111) alloys and their corresponding desorption temperatures. Throughout the remainder of this paper, all of the structural characterizations using XPD, ALISS, and XPS were done using a Zn/Pt(111) alloy surface that was formed by annealing a monolayer of Zn on Pt(111) to 600 K for 2 min, except where indicated otherwise.

3.2. Characterization of the PtZn Alloy. 3.2.1. XPD. Results from the clean Pt(111) surface are given and discussed as an important reference for characterizing the Pt–Zn alloy. Figure 5A shows a top view of the Pt(111) fcc crystal and
corresponding azimuthal directions. A side view of the [-12-1]/[1-21] azimuthal cross-section of the Pt(111) crystal is shown in Figure 5B. This azimuthal cross-section is identical to that of [2-1-1]/[-211] and [-1-12]/[11-2], because the fcc(111) single crystal has 120° rotational symmetry. This diagram shows several specific polar angles $\psi$ that correspond to enhanced photoemission intensity positions in the XPD data, as shown in the stereographic projection pattern presented in Figure 6. For example, Figure 6 exhibits enhanced emission intensity for a polar scan along the [-12-1] azimuth at $\psi = 0°, 19.5°, 35.3°,$ and $54.7°$. The left-hand side of Figure 5B attributes these peaks to electrons emitted from fourth-, third-, fourth-, and second-layer atoms, respectively. These emission directions correspond to the [111], [121], [141], and [010] vectors, respectively, projected on the hemispherical XPD pattern. The right-hand side of Figure 5B assigns the origin of the intensity enhancements for polar angles along the [1-21] azimuth (identical to the [2-11] azimuth) at $\psi = 0°, 10.0°, 35.3°,$ and $70.5°$. These peaks are attributed to electrons emitted from the fourth-, fifth-, second-, third-, and second-layer atoms, respectively, and correspond to the [111], [323], [101], [3-23], and [1-11] vectors, respectively, projected on the hemispherical XPD pattern, as marked in Figure 6. Some slight shifts were observed between the enhanced intensity directions measured in XPD and the calculated polar angle positions. This is partly due to mixing in enhanced emission that arises from deeper atoms which have similar, but not identical, polar angles. Figure 6 shows that both the polar and azimuthal directions of the Pt(111) single crystal can be identified unambiguously by observing the full-hemisphere XPD pattern.

As mentioned above, Figure 6 shows an image plot of a full-hemisphere XPD pattern for the Pt(111) crystal by stereographic projection. This plot was obtained by measuring the Pt 4$f_{7/2}$ and 4$f_{5/2}$ intensities along a given azimuthal direction, performing polar scans every 3° from $\psi = 0°$ to $75°$. Then the azimuthal direction was varied in 3° steps from $\phi = 0°$ to $120°$ while performing the same polar scans. For fcc(111) single crystals, the full-hemisphere XPD plot has 120° rotational symmetry. Therefore, data for only one-third of the full hemisphere is needed to map the entire pattern. Actually, one-sixth of the data would be enough to map the entire pattern if the polar scans were to start from the long azimuthal direction, for example, from [-12-1] to [-211]. This is because the full-hemisphere XPD plot has a mirror-symmetry plane every 60°. We collected the extra data, that is, one-third of the full hemisphere, to confirm the mirror and rotational symmetry planes and calibrate the sample alignment. As described above, specific features with enhanced intensity are labeled in Figure 6 and correspond to electron emission from specific layers of the crystal. Usually, the shorter the internuclear distance between scattering centers, the stronger the diffraction signal.
Figure 7 shows XPD polar scans of the Zn/Pt(111) alloy along the [-12-1] azimuth. The Pt 4f polar scans have four peaks near $\psi = 0, 19.5, 35.3,$ and $54.7^\circ$ corresponding to forward scattering from the fourth-, third-, fourth-, and second-layer Pt atoms, respectively. This result is identical to that for the clean Pt(111) crystal shown in Figure 5. This establishes that Pt atoms remain at the same, unchanged positions from the bulk termination of Pt(111) after forming the Zn/Pt(111) alloy. For the Zn 2p$_{3/2}$ XPD polar scans, an enhanced diffraction peak exists only near $\psi = 54.7^\circ$ which corresponds to Zn atoms occupying Pt sites in the second layer, although we can see the Zn 2p$_{3/2}$ peak in XPS at every polar angle. This suggests that some Zn atoms remain in the topmost layer and some migrate into the subsurface region, but these only significantly occupy second-layer sites, after forming the Zn/Pt(111) alloy.

Zn has a much lower surface free energy compared to Pt. As shown by the TPD results, upon annealing this leads to desorption of Zn atoms from the Zn/Pt(111) alloy formed in the near surface rather than diffusion of Zn deep into the substrate. This is further confirmed by the absence of a Zn signal after the alloy was sputtered at room temperature and subsequently annealed to temperatures ranging from 300 to 1200 K in 100-K increments. This behavior is different from that observed for the Sn/Pt(111), Ge/Pt(111), and Cu/Pt(111) bimetallic systems, where Sn, Ge, or Cu atoms migrate into the bulk of the crystal during annealing the substrate to form the alloys. Alloyed Zn can be easily removed from the Pt(111) surface by annealing the crystal up to 1200 K without sputtering.

3.2.2. ALISS. Because the scattering angle $\theta$ is fixed at $144^\circ$, the ratio between the scattered ion energy ($E_i$) and incident ion energy ($E_0$) is dependent only on the mass ratio between target atom ($m_2$) and projectile ion ($m_1$) according to

\[ \frac{E_i}{E_0} = \frac{m_1}{m_2} \]
Therefore, the mass \( m_2 \) of all surface atoms (with \( m_2 > m_1 \) in our geometry) can be determined by measurement of the peak positions in the ALISS energy scan. Figure 8 gives an energy spectrum of 1 keV Na\(^+\) ion scattered from the Zn/Pt(111) alloy along the [-12-1] azimuth at a polar angle of \( \Psi = 20^\circ \). The scattering angle \( \theta \) was fixed at 144\(^\circ\). The presence of this feature does not affect our analysis of the Zn or Pt intensity.

The presence of this feature does not affect our analysis of the Zn or Pt intensity. At some other angles, a minor feature appears at higher energies from the Pt single-scattering peak, which originates from double-scattering. Two separate scattering events lead to less total energy loss than one scattering event through the same total scattering angle.\(^{38,39}\) Figures 9–11 compare polar angle scans for 1 keV Na\(^+\) ions scattered from Pt atoms for clean Pt(111) and the Zn/Pt(111) alloy along [-12-1], [-211], and [-110] azimuths, respectively. In Figure 9, the scans for clean Pt(111) and the Zn/Pt(111) alloy along the long azimuth [-12-1] are not significantly different. At very low polar angle \( \Psi \), there is no Pt-scattering intensity. A peak near 20\(^\circ\) is attributed to scattering from Pt atoms in the first-layer and the peak near 58\(^\circ\) is due to scattering from Pt in the second layer.\(^{31,40,41}\) This can be visualized by looking at the cross section of the [-12-1] azimuthal direction for fcc(111) crystals shown in Figure 12. For ALISS, the polar angle \( \Psi \) is defined such that \( \Psi = 0^\circ \) corresponds to a direction parallel to the crystal surface plane. At low polar angles \( \Psi \), all the surface atoms in a "chain of
atoms” along the [-12-1] azimuth are hidden inside the “shadow cone” created by the proceeding atom in the chain. Therefore, no Pt scattering intensity is observed at very small values of $\Psi$. As the polar angle is increased, the first-layer atoms emerge from the shadow cone at a critical angle $\Psi_c$, but the shadow cones will prevent ion penetration to scatter from second-layer and deeper atoms. Thus, at a relatively low angle, which is near 20° for this azimuth on Pt(111) there is a peak in the scattering intensity due to scattering from atoms in the outermost layer. As the polar angle is further increased to $\Psi_2$, second-layer atoms emerge from the shadow cones created by the first layer atoms. Thus, the higher angle peak observed near 58° originates from second-layer Pt scattering. Along the [-12-1] azimuth, the third-layer atoms are still inside the first-layer shadow cones even if the polar angle is increased to $\Psi_3$, close to 90°, and thus, no third-layer scattering feature appears.

Figure 10, shows the ALISS scans for Pt on the clean Pt(111) surface and the Zn/Pt(111) alloy along the [-211] azimuth; the two scans are nearly identical, indicating little difference in structure of the Pt atoms between the two surfaces. As mentioned previously, the atomic structure along the [-211] azimuth is identical to the [1-21] direction and the mirror image of the [-12-1] azimuth. A cross section along the [-211] azimuthal direction for fcc(111) crystals is shown in Figure 13.

Along this azimuth, as with the scans on the [-12-1] azimuth, there is a critical angle for first-layer scattering near 20°. However, the second-layer scattering peak does not occur at 58° (shown as $\Psi_3$) as was observed in the [-12-1] azimuth. An increase in scattering intensity was observed at $\sim$86°, $\Psi_4$ in Figure 13, which is due to scattering from second or possibly third layer atoms emerging from the shadow cone created by surface layer atoms. It should be noted that the [-12-1] azimuth can be distinguished unambiguously from the [-211] azimuth by the different positions of the higher polar angle peaks originating from second layer scattering due to the different distance and angle between surface and second layer atoms in the two azimuthal directions.

Figure 11 shows that there was no differences between polar scans for clean Pt(111) and the Zn/Pt(111) alloy along the short azimuth [-110]. The low angle peak near 30° originates from first-layer Pt atoms.
features along the [-12-1] azimuth have a similar angular profile and peak positions to the Pt scattering features shown in Figure 9. If Zn atoms were present as dispersed adatoms in an overlayer, the Zn first-layer scattering peak would be at a lower angle than that of the Pt first-layer scattering peak near 20°. Therefore, the results in Figure 14 establish that Zn atoms are substitutionally incorporated into the topmost layer to form an alloy rather than remaining in an adlayer. The observation of a second-layer Zn-scattering peak at a similar position to that of the second-layer Pt-scattering peak indicates that Zn is alloyed not only into topmost layer but is present also in the second layer along with Pt. This is consistent with the conclusions from the Zn 2p3/2 polar scans in XPD presented in Figure 7. Nevertheless, the first-layer Zn scattering peak is higher than that of the second-layer Zn-scattering peak, contrary to that observed for Pt scattering, and this shows that that are more Zn atoms alloyed with Pt in the topmost layer than in the second layer. Zn scattering along the [-211] azimuth in Figure 14 shows a much smaller peak at 86° than that observed at 58° along the [-12-1] azimuth. As discussed earlier, this peak location is associated with second layer scattering in Pt(111) or possibly even third layer atoms. The smaller relative size of 86° Zn scattering peak along the [-211] compared to the peak observed at 58° along the [-12-1] azimuth could possibly indicate lower concentrations of Zn in the third layer compared to the second layer. This is also consistent with the XPD results. Both the ALISS and XPD data establish that Zn–Pt forms a bilayer alloy after annealing a one-monolayer Zn film on Pt(111) at 600 K.

Zn scattering features along the [-12-1], [-211], and [-110] azimuths in Figure 14 have the same first-layer scattering peak positions, as shown in Figures 9–11, respectively, for Pt-scattering features. These also confirm that Zn atoms are substitutionally incorporated into the topmost layer to form an alloy rather than an adlayer.

The ALISS data can also be used to quantitatively determine the Zn concentration in the topmost layer of the alloy. The scattered ion intensity at Ψ = 40° along the [-211] azimuth shows little dependence on small changes in polar angle making this region best suited for quantitative determination of surface composition. Thus, the Zn concentration can be determined using the ion scattering intensities measured for Zn and Pt at these angles for the Zn/Pt(111) alloy, and the following relationship:

\[ C_{Zn} = \frac{I_{Zn}/S_{Zn}}{I_{Zn}/S_{Zn} + I_{Pt}/S_{Pt}} \] (2)

The sensitivity factors were evaluated using ALISS spectra taken at the same conditions for clean Pt(111) and a thick Zn film (where no Pt scattering was observed). This determined that \( S_{Zn} = 3.4 \) and that \( C_{Zn} = 0.05 \) ML in the first atomic layer with the remaining Zn alloying in the near surface region.

Quantitative analysis by XPS gave a consistent answer for the Zn concentration in this alloy. The Zn XPS signal was directly compared to the Ge XPS signal obtained for the \( (\sqrt{19}x\sqrt{19}) \) R23.4°-Ge/Pt(111) surface alloy, which contains 0.056 ML Ge in the top layer.23 Using the tabulated22 relative sensitivity factors for Zn and Ge in XPS, it was found that the composition of Zn at the surface was also quite dilute, about 5%, supporting the ALISS determination.

3.2.3. Critical Angle. The critical angle Ψc in an ALISS polar scan is normally assigned at 90% of the peak maximum for the scattering feature.18,21 The first-layer scattering features of Pt (from clean Pt(111) and the Zn/Pt(111) alloy) and Zn (from the Zn/Pt(111) alloy) along the [-12-1] azimuthal direction are shown in Figure 15. The critical angles Ψc are 19.0, 19.0, and 19.1°, respectively. The relative position of Zn and Pt atoms can be determined by comparing the corresponding Ψc values.16,18,21,30,31,40 The critical angle of the first-layer Pt scattering peak from clean Pt(111) is unchanged after alloying with Zn to form the Zn/Pt(111) surface alloy. This ordinarily would be sufficient to establish that the average position of first-layer Zn atoms is coplanar with the Pt atoms in the Pt(111) surface without any buckling. But, because of the dilute concentration of Zn, most of the surface Pt atoms are still surrounded by other Pt atoms and any buckling effect might not be indicated by an altered critical angle. Therefore, we need
additional information to prove that there is no buckling for the alloyed Zn atoms.

This evaluation comes from comparing the critical angles of first-layer Pt and Zn scattering peaks from the Zn/Pt(111) alloy. They have almost the same values of 19.0 and 19.1°. In a dilute alloy, nearly all of the Zn atoms will be surrounded by Pt atoms. If Zn is buckled outwardly from the Pt surface plane, the critical angle of the Zn scattering peak should be lower than that of the Pt scattering peak at 19.0°. On the contrary, if Zn is buckled inwardly from the Pt surface plane, the critical angle of the Zn scattering peak should be higher than that of the Pt scattering peak. We find no significant difference between these two critical angles, confirming that surface Zn and Pt atoms are located in the same plane without any buckling. Importantly, identical results to that of the [-12-1] azimuth were obtained in the other two azimuthal directions, [-211] and [-110].

This result is consistent with previous data which showed a linear relationship between the lattice mismatch and buckling distance for bimetallic alloys of Sn with fcc metals.21,30 Zn and Pt have nearly the same atomic radii of 1.37 and 1.39 Å, respectively, and no buckling would be expected for Zn atoms in the surface plane of a Zn/Pt(111) alloy if this behavior were general.

3.2.4. Chemical Probes. In addition to ion scattering and XPD, chemical probes (O2, CO, and NO) were used to characterize the surface of the Zn/Pt(111) alloys. The propensity for the surface to become oxidized upon exposure to O2 was studied using XPS. The upper portion of Figure 16A displays the X-ray induced L3M45M45 Auger peaks for the 1 ML Zn/Pt(111) sample before and after exposure to 50 L O2.

Figure 16. X-ray induced L3M45M45 Auger peak locations of (top) 1 ML of PtZn alloy on Pt(111) and (bottom) 1 ML of Zn adatoms on Pt(111) before and after exposure to 50 L O2.

Figure 16B, this is in contrast to a 1 ML Zn adatoms on Pt(111) that had not been annealed to 600 K to induce alloy formation. For this sample, oxidation of Zn is readily apparent upon exposure to O2 and causes a 0.5 eV downward shift in the primary Zn Auger peak43-46. In light of the strong affinity of Zn for oxygen,47-49 it is somewhat surprising that the Zn/Pt(111) surface alloy is relatively unreactive. This could be due to a high thermodynamic stability for the Zn/Pt(111) alloy or the fact that only a small fraction of the Zn is present in the outermost surface.

Because the bonding of CO to metal surfaces is very sensitive to the electronic structure, especially the d-band energy and occupancy, CO TPD was used to characterize the effect of alloying on the electronic properties of the surface. CO is known to preferentially bind the carbon end down on the top sites at low coverage on Pt(111).50-53 In this configuration bonding occurs via transfer of electron density from the filled CO σ orbital into the Pt 5d2 orbital and back-donation from the Pt 5dσ and 5dπ orbitals into the unoccupied CO 2π antibonding orbital. It has previously been proposed that alloying with Zn causes a decrease in the electron density in the Pt d band.2,13,35 Thus, one might expect that alloying Pt with Zn would decrease the amount of back-donation into the CO 2π orbital resulting in a destabilization of the adsorbed CO. The CO TPD data in Figure 17 show that this is indeed the case. These data were obtained from Zn/Pt(111) alloy surfaces at 100 K dosed with 0.1 L of CO as a function of the Zn concentration in the near surface alloy. Note that the CO desorption peak shifts from 475 K on the Zn-free Pt(111) surface to 360 K for the 1 ML Zn/Pt(111) alloy surface. The CO sticking coefficient was also found to decrease with increasing amount of Zn in the bimetallic alloy surface. Similar results were obtained for the interaction of NO with the alloy surface. In this case, the destabilization was such that NO was found to not adsorb on the Zn/Pt(111) alloy surface above room temperature. These data show that in spite of the fact that the Zn concentration in the top two layers of the Zn/Pt(111) alloy surface is relatively small (<0.1 ML), the surface is chemically very distinct from that of Pt(111).

Figure 17. TPD Spectra following 0.1 L CO dosage on Zn/Pt(111) surface at 120 K as a function of Zn coverage.
4. CONCLUSIONS

A considerable range of conditions were explored in order to search for formation of long-range ordered structures by depositing Zn on a Pt(111) single-crystal substrate. No such structures were found. Zn alloys with Pt upon annealing, and we have used XP and ALISS to characterize the PtZn alloy created by annealing one monolayer of Zn on Pt(111) to 600 K. This PtZn/Pt(111) alloy had a diffuse (1 × 1) LEED pattern, suggesting the formation of a random, substitutional alloy between Pt and Zn. The Zn concentration in the surface layer of this alloy was determined by ALISS and XPD to be 0.05 ML. Both XP and ALISS results establish that, under these conditions, Zn alloys with Pt primarily on the topmost and second layer to form a bilayer alloy. ALISS polar scans show that Zn atoms are substitutionally incorporated into Pt lattice positions. Alloyed Zn atoms in the surface layer are located coplanar with the surface Pt atoms, without any vertical displacement or “buckling”. This is consistent with existing trends observed for Sn alloys with late transition metals that would predict no buckling based on the nearly identical atomic radii of Zn and Pt of 1.37 and 1.39 Å, respectively. Upon further annealing to 850 K, Zn atoms desorb from the Pt(111) surface rather than diffuse into the substrate. TPD results show that both CO and NO chemisorb more weakly on the Zn/Pt alloy surface compared to that on the clean Pt(111) surface, with NO more strongly affected. No NO adsorption occurs on this Zn/Pt alloy surface under UHV conditions at 325 K.

As a final note, we mention that several previous papers misidentified the [−12·1] and [−211] azimuths in ALISS results, and we show how these can be distinguished by the different angles where scattering intensity peaks were observed in ALISS measurements.

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The authors declare no competing financial interest.

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