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Growth and structure of Pd films on ZnO(0001)

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The growth and structure of Pd films on ZnO(0001) were investigated using high resolution electron energy loss spectroscopy, x-ray photoelectron spectroscopy, and low energy electron diffraction. Vapor deposited Pd films at 300 K were found to follow a two-dimensional (2D) island growth mode, in which 2D metal islands are formed up to a critical coverage at which point growth occurs primarily in a layer-by-layer fashion on top of the islands. Heating to only 350 K was found to be sufficient to induce partial agglomeration of Pd films into three-dimensional particles. In addition to causing further agglomeration into particles, heating to 700 K resulted in partial reduction of the ZnO surface and the formation of a PdZn alloy. © *2006 American Institute of Physics*.
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I. INTRODUCTION

Steam reforming of methanol (SRM) [$CH_3OH+H_2O \rightarrow CO_2+3H_2$] has recently received much attention as a method to produce H_2 for use in proton exchange membrane fuel cells (PEMFC).[1–3] Copper supported on ZnO is a well known catalyst for this reaction and while it exhibits high activity and selectivity it has several shortcomings including being pyrophoric upon reduction and subject to deactivation at temperatures above 550 K where the Cu sinters. In efforts to find more robust SRM catalysts, supported group VIII metals have been investigated.[4–7] While supported Pt and Pd catalysts exhibit high activity, they are generally selective for the production of CO and H_2 rather than CO_2 and H_2.[4] This is not desirable since the CO must be converted to CO_2 and H_2 via the water gas shift reaction. One exception to this is Pd supported on ZnO, which has been found to have exceptionally high selectivity for the production of CO_2 and H_2 during SRM.[4,5] To obtain high SRM activity Pd/ZnO catalysts must be reduced at temperatures above 573 K, and it is generally accepted that this causes partial alloying of the Pd with Zn.[4,5] While it is clear that PdZn alloy formation is important, many questions regarding the structure of the active form of the catalyst and the nature of the synergistic interactions between Pd and the ZnO support remain poorly understood. In order to provide fundamental insight into the interaction of Pd with ZnO and how these interactions affect catalytic activity, we have recently begun to investigate the structure and reactivity of model catalysts consisting of vapor deposited Pd films supported on the (0001) surface of a ZnO single crystal. In this paper we report the results of a study in which high resolution electron energy loss spectroscopy (HREELS), x-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED) were used to characterize the growth, structure, and thermal stability of Pd films on ZnO(0001). The reaction of CH_3OH on Pd/ZnO(0001) model catalysts will be the subject of a future publication.

ZnO has a wurtzite lattice and the (0001) surface consists of a hexagonal array of Zn^{2+} cations in the outermost layer and a subsurface layer O^{2-} anions. There have been several previous studies of the growth of metal films on both the ZnO(0001) and ZnO(000$\bar{1}$) surfaces [the (000$\bar{1}$) surface is terminated with oxygen rather than Zn].[8–15] These studies show that vapor deposited Cu and Pt films follow a two-dimensional island (2DI) growth mode, in which two-dimensional (2D) metal islands are formed up to a critical coverage at which point growth occurs primarily in a layer-by-layer fashion on top of the islands.[16] Alloying of Cu and Pt with Zn supplied by the substrate was not observed in these studies. There have also been several previous studies of Pd films on ZnO single crystal surfaces.[17–20] For example, Gaebler *et al.*[17] investigated vapor deposited Pd films on ZnO(0001) and ZnO(000$\bar{1}$) using Auger electron spectroscopy (AES) and ultraviolet photoelectron spectroscopy (UPS) and reported that the films grew in a layer-by-layer fashion on both surfaces. These results are in contrast to those of Jacobs *et al.*,[18] who reported based on AES and LEED data that vapor deposited Pd forms three-dimensional (3D) clusters on the ZnO(000$\bar{1}$) surface. Neither of these previous studies investigated the possibility that Pd reacts with the ZnO surface to form a PdZn alloy. As will be shown below, the HREELS, XPS, and LEED results obtained in the present study provide a more detailed description of the structure and thermal stability of Pd films on ZnO(0001) and help identify the conditions for which the Pd reacts with the ZnO surface to form a PdZn alloy.

II. EXPERIMENT

All experiments were conducted in two separate ultrahigh vacuum (UHV) surface analysis chambers with background pressures of $\sim 2\times 10^{-10}$ Torr. Both chambers were equipped with an ion sputter gun (Physical Electronics) for

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sample cleaning, a quadrupole mass spectrometer (UTI) for TPD studies, and a quartz crystal oscillator (Maxtek, Inc.) for monitoring the flux from the palladium metal deposition source. One of the chambers contained an LK Technologies model 3000 HREEL spectrometer and a retarding field electron energy analyzer (OCI Vacuum Microengineering) that was used for both AES and LEED. The other system contained a hemispherical electron energy analyzer (Leybold-Heraeus) and an x-ray source (VG Microtech), which were used for XPS.

The ZnO(0001) single crystal substrate used in this study was approximately $6\times6\times1$ mm in size and was mounted in a tantalum foil holder that was attached to the sample manipulator on the UHV chamber. The sample temperature was monitored using a Chromel-Alumel thermocouple that was attached to the back surface of the ZnO crystal using a ceramic adhesive (Aremco). The sample was heated via conduction from the resistively heated tantalum foil holder. The ZnO(0001) surface was cleaned using repeated cycles of sputtering with 2 kV Ar^+ ions followed by annealing at 875 K. The sputter/anneal cycles were repeated until the surface was free from carbon and other impurities as determined by AES or XPS.

A resistively heated evaporative metal source was used for Pd deposition and was constructed by wrapping 0.127 mm diameter high purity Pd wire (Alfa Aesar, 99.9%) around a 0.2 mm diameter tungsten wire. The tungsten wire was then attached to an electrical feedthrough on the UHV chamber allowing it to be heated resistively. The steady state flux of Pd was monitored using the quartz crystal film thickness monitor. Pd deposition was conducted with the ZnO(0001) sample at 300 K with a growth rate of $\sim$0.2 Å s^{-1}. We report the Pd coverages in monolayers (ML), where 1 ML of Pd is defined as 1.53×10^{15} atoms cm^{-2}, which is the packing density in the Pd(111) surface.

HREELS data were collected in the specular direction using a 4 eV incident electron beam directed 60° from the surface normal. XP spectra were collected using an Al $K\alpha$ x-ray source (1486.6 eV) and the binding energies were referenced with respect to the Zn($2p_{3/2}$) peak at 1021.7 eV.[21]

III. RESULTS

A. Pd film growth

HREELS was initially used to characterize the growth of vapor deposited Pd layers on ZnO(0001). The HREEL spectra of metal oxides are dominated by losses resulting from the excitation of the Fuchs-Kliewer, long wavelength, optical phonon modes of the lattice. As has been shown in previous HREELS studies,[11,22] the conduction electrons in metal overlayers are highly effective at screening the oscillating dipole moment of the phonon mode of the substrate causing rapid diminution of the phonon peak intensity in the HREEL spectrum with metal film thickness. Indeed, a single monolayer of metal can cause almost complete shielding of the phonon mode from the incident electron beam.[11] Thus, HREELS is a sensitive tool for characterizing the growth mode and structure of metal overlayers on oxide single crystals.

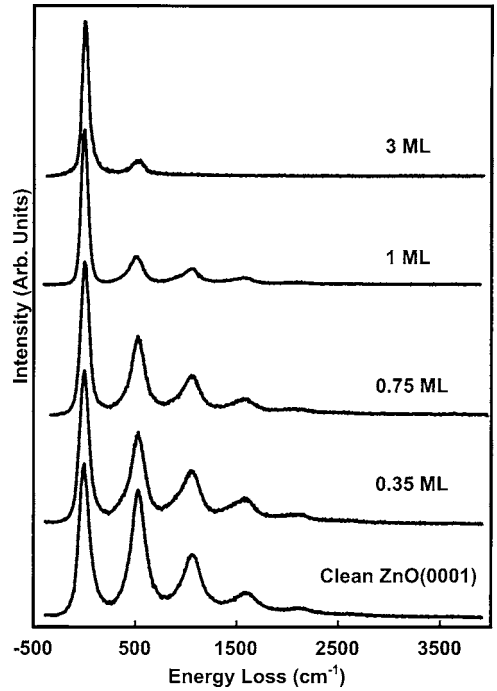

FIG. 1. HREEL spectra of Pd/ZnO(0001) sample as a function of Pd coverage.

Figure 1 displays the HREEL spectrum of ZnO(0001) as a function of the amount of Pd deposited on the surface. The bottommost spectrum in this figure is from the clean ZnO(0001) surface and contains a large peak at 528 cm^{-1} corresponding to the optical phonon mode of the ZnO lattice. A series of progressively smaller peaks which occur at integer multiples of the phonon energy (i.e., 1056, 1584, and 2112 cm^{-1}) is also present in the spectrum. These are phonon-phonon combination peaks resulting from sequential excitation of the phonon mode by a single incident electron. The spectrum is in good agreement with those reported previously for ZnO(0001).[11,23–25]

The remaining spectra in Fig. 1 were obtained following deposition of 0.35, 0.75, 1, 1.5, and 3 ML of Pd. As expected, the Pd film shields the oscillating dipole moment of the ZnO phonon mode from the electron beam and causes a reduction in the intensity of phonon losses without changing their positions. This is further illustrated in Fig. 2, which displays the ratio of the intensity of the primary phonon peak to that of the elastic peak. This ratio decreases from a value of 0.83 for the clean surface to 0.11 after deposition of 3 ML of Pd. This rapid decrease with coverage indicates that the Pd film covers a significant fraction of the surface. As will be discussed below, the trend is not consistent, however, with a complete layer-by-layer growth mode since a 3 ML film would be expected to completely shield the phonon mode from the incident electron beam.

The electronic structure and morphology of the vapor deposited Pd film on ZnO(0001) surface were also investigated by XPS. Figure 3 displays Pd($3d$) core level spectra as a function of the Pd coverage. For the 0.35 ML Pd film, the Pd $3d_{5/2}$ and $3d_{3/2}$ peaks are centered at 335.4 and 340.6 eV, respectively. These peak positions are consistent with those

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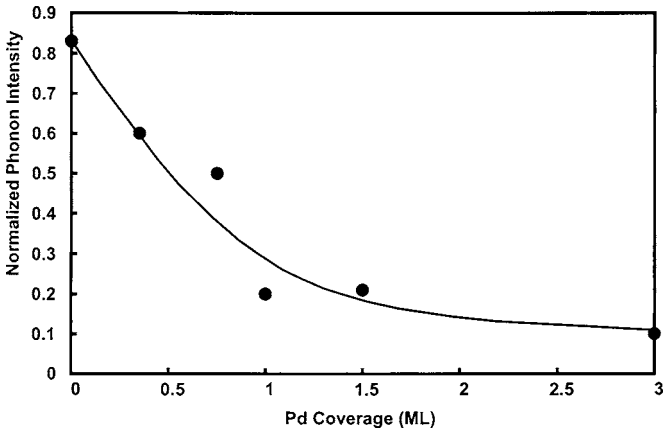

FIG. 2. Ratio of the intensity of the primary ZnO phonon peak in the HREEL spectrum to that of the elastic peak as a function of the Pd coverage for Pd/ZnO(0001).

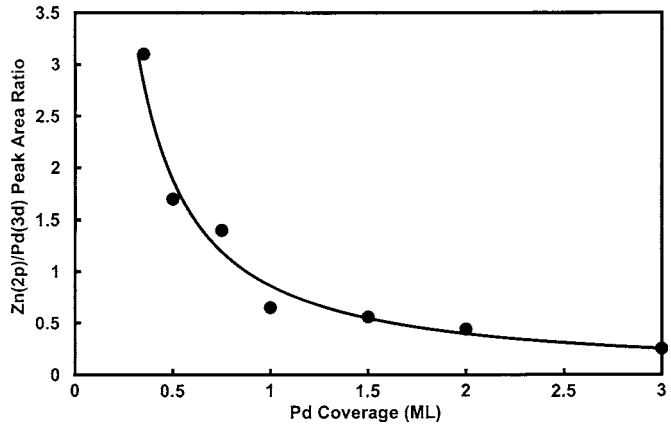

FIG. 4. Ratio of the areas of the Zn(2*p*) core level peaks to that of the Pd(3*d*) core level peaks in the XPS spectra as a function of the Pd layer thickness for Pd/ZnO(0001).

reported for metallic Pd.[21] The peaks shift to slightly lower binding energies with increasing Pd coverage and for the 3 ML film the Pd $3d_{5/2}$ and $3d_{3/2}$ peaks are centered at 334.9 and 340.1 eV, respectively. This decrease in binding energy with coverage is consistent with results reported previously by Leighton *et al.*[20] and can be attributed to charge transfer at the Pd-ZnO interface.

A plot of the ratio of the areas of the Zn(2*p*) peaks to those of the Pd(3*d*) peaks as a function of Pd coverage is shown in Fig. 4. Similar to the HREELS data, this ratio decreases rapidly with Pd coverage going from 3.1 for the 0.35 ML film to only 0.2 for the 3 ML film. This result again indicates that vapor depositing Pd at 300 K produces a film that covers most of the ZnO surface, rather than large Pd particles.

LEED was also employed to characterize the structure of the Pd layers on ZnO(0001) surface. Figure 5(a) shows LEED pattern of clean ZnO(0001) surface obtained with an incident electron beam energy of 70 eV. The LEED pattern displays hexagonal symmetry as is expected for this surface, which consists of (1×1) hexagonal array of Zn^{2+} cations with nearest neighbor spacing of 3.25 Å. This pattern agrees well with those reported in the literature.[26,27] The LEED pattern obtained after depositing 3 ML of Pd is displayed in Fig. 5(b). Note that the hexagonal pattern of the ZnO(0001) substrate is still observed; however, the pattern has become much more diffuse. This result is similar to that reported previously for Pt layers on ZnO(0001).[11]

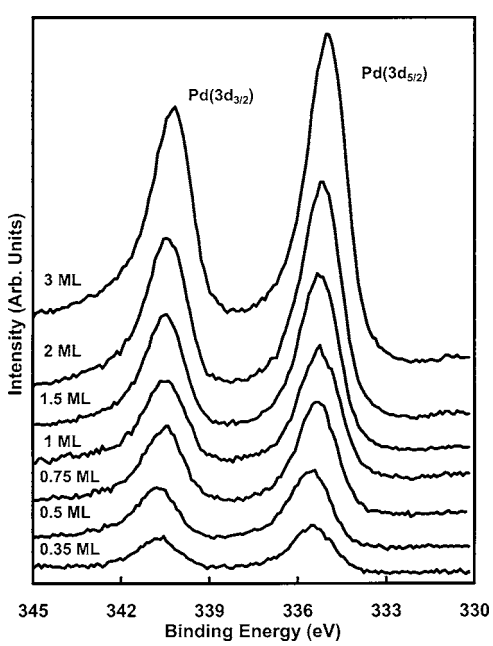

FIG. 3. XP spectra of the Pd(3*d*) peaks for Pd/ZnO(0001) as a function of Pd coverage.

B. Thermal stability and PdZn alloy formation

The thermal stability of Pd overlayers on ZnO(0001) was studied using HREELS, XPS, and LEED. In these experiments ZnO(0001) substrates covered with 0.5 and 3 ML Pd films were annealed to a series of progressively higher temperatures for 1 min at which point they were cooled to room temperature and HREELS, XPS, and LEED data were collected. Figure 6 shows a plot of the ratio of the intensity of the primary phonon peak in the HREEL spectrum to that of the elastic peak as a function of annealing temperature for a 3 ML Pd film on ZnO(0001). A subset of the HREEL spectra collected in this series of experiments is displayed in Fig. 7 along with that of the clean ZnO(0001) surface for comparison. The data in these figures show the reemergence of the phonon peaks of the ZnO substrate with increasing annealing temperature. Note that the intensity ratio goes from 0.1 for the as-deposited film at 300 K to 0.7 after annealing at 850 K. This latter value is only 0.13 less than that obtained from the clean ZnO(0001) surface. These results demonstrate that more of the ZnO(0001) surface becomes exposed upon annealing and consequently the Pd film must be agglomerating into particles. It is also noteworthy that agglomeration of the Pd film starts to occur at relatively low temperatures and an increase in the phonon to elastic peak ratio is observed after heating to only 350 K. This result is in contrast to that reported previously for Pt on ZnO(0001), where temperatures in excess of 600 K were required in order to induce agglomeration of vapor deposited Pt films,[11,12] and suggests that Pd interacts much more weakly with this

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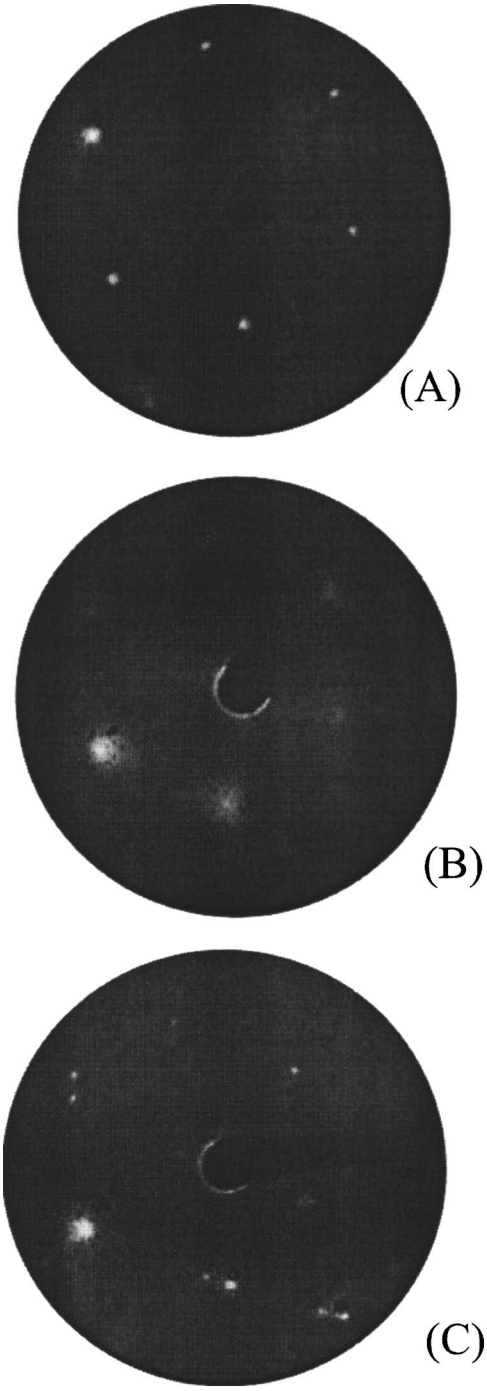

FIG. 5. LEED patterns of (A)clean ZnO(0001), (B) 3 ML Pd film on ZnO(0001) at 300 K, and (C) following annealing of the film in (B) at 850 K.

surface than Pt.

XPS results also demonstrate agglomeration of the Pd layer upon heating. Figure 8 shows the ratio of the area of Zn(2*p*) peaks to that of the Pd(3*d*) peaks as a function of annealing temperature for ZnO(0001) covered with 0.5 and 3 ML Pd films. For the 3 ML Pd sample, the Zn(2*p*)/Pd(3*d*) peak area ratio increases upon heating to only 350 K and continues to increase for annealing temperatures up to 900 K. This result agrees well with the HREELS data and again suggests a weak interaction between Pd and the ZnO(0001) substrate. In the case of the 0.5 ML Pd film the

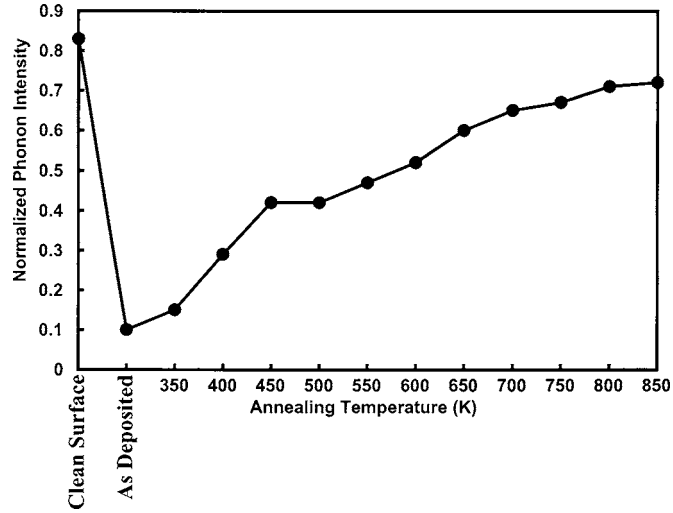

FIG. 6. Ratio of the intensity of the primary ZnO phonon peak in the HREEL spectrum to that of the elastic peak as a function of annealing temperature for 3 ML Pd on ZnO(0001).

area ratio increases for annealing temperatures up to 500 K, is relatively constant between 500 and 750 K, and increases markedly upon heating to 900 K.

More detailed analysis of the Pd(3*d*) core level XPS spectra shows that in addition to agglomeration into particles, upon annealing, the Pd reacts with the ZnO(0001) surface resulting in the formation of a PdZn alloy. This is shown in Fig. 9, which displays Pd(3*d*) XPS spectra for a 0.5 ML Pd film on ZnO(0001) as a function of annealing temperature. In the spectrum of the as-deposited film at 300 K, the Pd($3d_{5/2,3/2}$) peaks are centered at 335.4 and 340.6 eV corresponding to Pd metal.[21] Upon annealing to 500 K these peaks shift 0.4 eV to lower binding energy and are centered at 335.0 and 340.2 eV. As noted above, heating to 500 K is sufficient to induce partial agglomeration of the Pd film. Thus, the peak shift can be attributed to the change in the morphology of the Pd film and again suggest that there may be a small amount of charge transfer at the Pd-ZnO interface. An additional 0.4 eV downward shift was observed for the primary Pd(3*d*) peaks upon heating to 700 K. Heating to this temperature also resulted in the emergence of shoulders on the sides of the Pd $3d_{5/2}$ and $3d_{3/2}$ peaks that are centered approximately 1 eV higher in energy than the primary peaks. The positions of these new features are approximately 1 eV lower than those reported in the literature for PdO.[28] Thus, it is not likely that they result from oxidation of the Pd layer. Formation of a PdZn alloy is another possible explanation for these new features. Rodriguez[29] has previously used XPS to characterize PdZn films deposited on Ru(001) and observed that alloying of Pd with Zn causes an increase in the binding energies of the Pd(3*d*) electrons. For example, for a PdZn film containing only 10% Zn, the Pd($3d_{5/2}$) peak was found to increase by 0.62 eV relative to that for pure Pd. Comparison to Rodriguez's results supports the assignment of the shoulders on the high binding energy sides of the Pd $3d_{5/2}$ and $3d_{3/2}$ peaks in the spectra of the 0.5 ML Pd/ZnO(0001) sample annealed at 700 K to a PdZn alloy. This assignment is also supported by previous XPS studies

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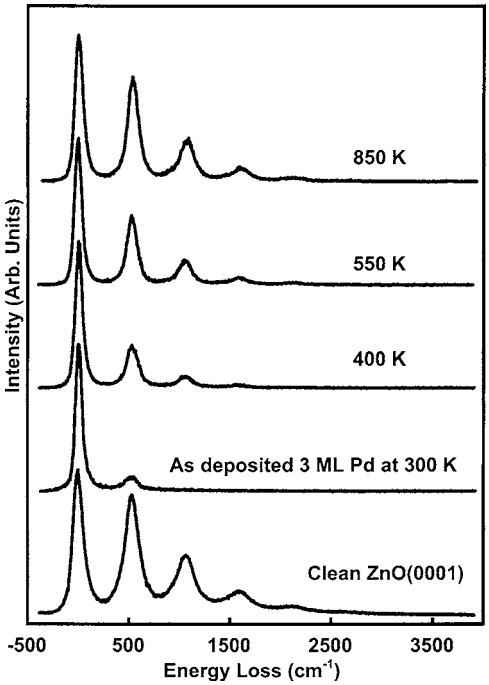

FIG. 7. HREEL spectra of 3 ML Pd film on ZnO(0001) at different annealing temperatures.

of high surface area Pd/ZnO catalysts. For example, Iwasa *et al.*[4–6] used XPS to characterize 10 wt % Pd/ZnO samples calcined in air at 773 K and reduced in H_2 at several different temperatures. They observed that the Pd $3d_{5/2}$ binding energy for the air calcined sample, which presumably contained only PdO, was 1.6 eV higher in energy than that for Pd metal in samples reduced in H_2 at temperatures below 500 K. Note that this shift is larger than that observed in the present study and again suggests that the shoulders that emerge on the sides of the Pd 3*d* peaks upon annealing the Pd/ZnO(0001) sample do not result from oxidation of the Pd. For a 10 wt % Pd/ZnO sample reduced in H_2 at 673 K, Iwasa *et al.* observed that the Pd(3*d*) peaks increased in binding energy by 0.6 eV relative to that for metallic Pd and assigned this shift to the formation of a PdZn alloy which was consistent with x-ray diffraction results. This magnitude of a shift is closer to that observed for the shoulders in the Pd 3*d* data obtained in the present study for Pd/ZnO(0001) samples heated to 700 K and higher and, therefore, provides further support for the assignment of these features to a PdZn alloy. The high binding energy shoulders became more prominent upon annealing the 0.5 ML Pd/ZnO(0001) sample to 800 and 850 K and further broadening of the peaks was observed upon annealing to 900 K, indicating that additional Zn was incorporated into the Pd deposits at the higher annealing temperatures.

A LEED pattern obtained after annealing the sample covered with 3 ML Pd to 850 K is displayed in Fig. 5(c). The diffraction spots in this pattern are considerably sharper that those in the pattern obtained prior to annealing, which is consistent with the Pd film agglomerating into particles. Also note that splitting of the diffraction spots is apparent. A similar result has been reported for annealed Pt films on ZnO(0001) (Ref. 11) and can be attributed to superposition

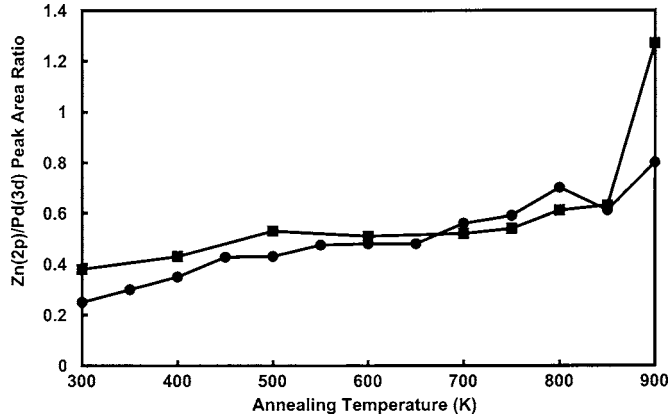

FIG. 8. Ratio of the areas of the Zn(2*p*) core level peaks to those of the Pd(3*d*) core level peaks in the XPS spectra. Ratio of the areas of the Zn(2*p*) core level peaks to those of Pd(3*d*) as a function of annealing temperature for ZnO(0001) covered with 0.5 ML (square) and 3 ML (circle) Pd films.

of the diffraction pattern from the ZnO(0001) substrate and that from the supported metal particles. The observation of the diffraction spots for the Pd or PdZn particles indicates that they are oriented with respect to the substrate.

IV. DISCUSSION

The trends in the HREELS and XPS data as a function of Pd coverage demonstrate that the vapor deposited Pd films on ZnO(0001) initially grow by the formation of 2D islands

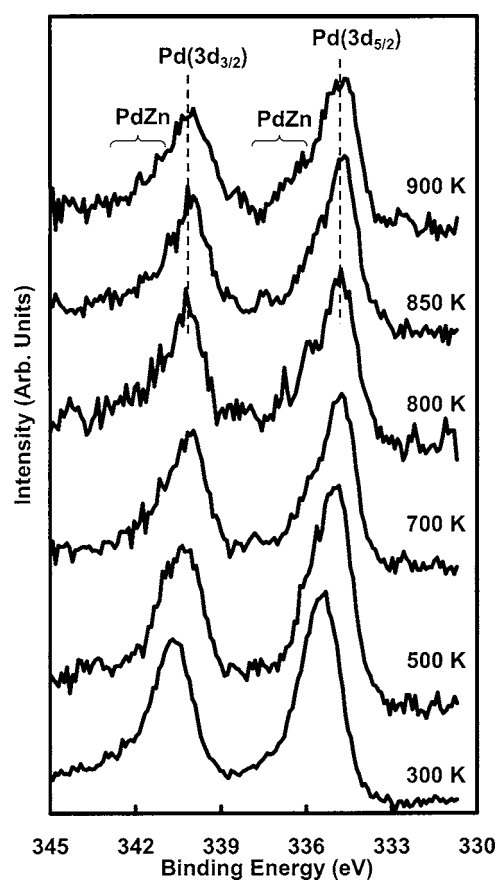

FIG. 9. Pd(3*d*) XPS spectra of 0.5 ML Pd on ZnO(0001) at different annealing temperatures.

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rather than 3D particles. The decrease in the substrate signals with Pd coverage is not consistent, however, with a true layer-by-layer growth mode. This becomes apparent when one compares the results of this study to our previous study of Pt film growth on ZnO(0001).[11] Using HREELS it was found that a Pt coverage equivalent to 2 ML was sufficient to completely shield the ZnO phonon mode in the HREEL spectrum. This is consistent with the Pt film being metallic and essentially covering all of the ZnO substrate. Note, however, that for Pd/ZnO(0001) a small ZnO phonon peak is still evident even for an equivalent 3 ML Pd film (Fig. 1). Since the shielding characteristics of Pd and Pt should be nearly identical, this result indicates that a portion of the ZnO surface is still exposed for this coverage.

It is useful to compare our results to those obtained in the previous studies of Pd films on ZnO surfaces. Gaebler *et al.*[17] were the first to study the growth of vapor deposited Pd films on single crystal surfaces of ZnO and based on analysis of AES data they concluded that the films grow in a layer-by-layer fashion on both ZnO(000$\bar{1}$) and ZnO(0001). In a later study Jacobs *et al.*[18] also used AES to determine the growth mode for vapor deposited Pd films on ZnO(000$\bar{1}$) and concluded that only one-half of the surface was covered for a 5 ML Pd film and that the film follows a Volmer-Webber cluster growth mode. Due to its relatively large sampling depth (~30 Å) and the need to know the electron mean free paths in the materials being analyzed, it is difficult to discern film growth modes using AES data alone. Thus, it is not particularly surprising that similar data led to different conclusions in these two studies. As will be discussed in detail below, our results are more consistent with the interpretation in the study of Jacobs *et al.* The HREELS results obtained in the present study provide additional insight, however, into film nucleation on the ZnO(0001) surface and the initial stages of film growth.

Comparisons of the results obtained in this study to those reported previously for the growth of vapor deposited Cu and Pt films on the (0001) and (000$\bar{1}$) surfaces of ZnO by Campbell and co-workers[8,9,12–15] provide additional insight into the structure and growth mode of Pd films on ZnO(0001). Campbell and co-workers showed using low energy ion scattering (LEIS), a technique that provides a quantitative measure of the fraction of the surface which is covered by the metal film, that at 300 K vapor deposited Cu and Pt on ZnO(0001) (Refs. 9 and 13) and Cu on ZnO(000$\bar{1}$) (Ref. 8) grow in a pseudo layer-by-layer mode, which they referred to as a 2DI growth mode. The 2DI growth mode is characterized by the initial growth of two-dimensional islands. Upon reaching a critical coverage, however, additional growth occurs primarily via layer-by-layer growth on top of the islands with filling in of the spaces between the islands occurring relatively slowly. This growth process is kinetically controlled and results in metastable films that agglomerate into particles upon heating. A detailed description of the conditions that are required for this growth mode can be found in the references.[16] The general concept, however, is that during the initial stages of growth the most energetically favorable adsorption site for a deposited metal atom is at the edge of a two-dimensional metal island, since this will maximize its number of nearest neighbors. Thus, if the metal deposition rate is slow and the deposited metal atoms have sufficient energy to overcome the barriers to lateral diffusion, 2D metal islands will be formed. As the islands become larger, the probability that a metal adatom on top of a 2D island will encounter a second metal adatom and nucleate in the second layer increases, and at a critical island size or coverage, layer-by-layer growth on top of the metal islands becomes dominant. The second layer edge sites also provide for an energetically accessible pathway for first layer metal atoms to "upstep" into the second layer. The net effect is that once the critical coverage is obtained, the lateral growth of the islands decreases and the islands primarily thicken upon deposition of more metal.

The XPS and HREELS data obtained in the present study for Pd on ZnO(0001) also appear to be consistent with a 2DI growth mode. While LEIS data are generally required in order to accurately determine the critical island coverage at which point the growth on top of the 2D islands dominates, comparisons to previous HREELS and LEIS studies of metal film growth on ZnO(0001) and ZnO(000$\bar{1}$) allow us to at least obtain a rough estimate of the critical coverage for the Pd/ZnO(0001) system. Using LEIS, Grant *et al.*[13] showed that at 300 K the growth of vapor deposited Pt films on ZnO(0001) occurs via the 2DI mode with a critical island coverage of 0.7. As noted above, in our studies of film growth on ZnO(0001) it was observed that a 1 ML Pt film was sufficient to nearly completely shield the phonon mode in the HREEL spectrum, while a phonon peak is still evident in the HREEL spectrum of a 3 ML Pd film on this surface. This result is consistent with the critical island coverage for Pd being somewhat less than that for Pt.

Both LEIS and HREELS have also been used to characterize the growth of Cu films on ZnO(000$\bar{1}$) surfaces. Campbell *et al.* showed using LEIS that the critical island coverage for Cu films grown at 300 K on ZnO(000$\bar{1}$) was only 0.35.[8] This low value is confirmed by the studies of Thornton *et al.*,[10] who used HREELS to characterize Cu film growth on ZnO(000$\bar{1}$). In that study it was observed that the phonon intensity in the HREEL spectrum decreased very slowly with Cu coverage. For an equivalent 1 ML Cu film the phonon intensity decreased by less than 10% and nearly an equivalent of 30 ML of Cu were required in order to completely shield the phonon. Comparison of these results to the HREELS data for Pd/ZnO(0001) leads to the conclusion that the critical island coverage for Pd is significantly larger than that for Cu. Based on these comparisons between the various HREELS and LEIS studies of metal film growth on ZnO and analysis of our XPS data we conclude that the critical island coverage for Pd on ZnO(0001) is between 0.5 and 0.6.

The lower value for the critical island coverage for Pd compared to Pt on ZnO(0001) suggests that the interaction energy of Pd with this surface is somewhat less than that for Pt. This conclusion is consistent with the studies of the thermal stability of Pd films deposited at 300 K. The HREELS and XPS data in Figs. 6 and 8 show that the Pd overlayers start to agglomerate upon heating to only 350 K. Similarly,

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Cu films on ZnO(0001) begin to thicken at only 450 K as reported by Yoshihara *et al.*[9] The low thermal stability of both Cu and Pd films on ZnO is in contrast to that of Pt. In our group's previous study of Pt/ZnO(0001),[11] it was shown that Pt overlayers are thermally stable up to 600 K and only start to agglomerate upon heating to higher temperatures.

Perhaps the most interesting observation in this study is that annealing Pd films on ZnO(0001) appears to result in partial reduction of the ZnO surface and the formation of a PdZn alloy. Alloy formation is suggested by the XPS data for both the 0.5 ML Pd film (Fig. 9) and for the 3 ML Pd film, where Pd(3*d*) peaks emerge at binding energies higher than those of pure Pd upon annealing the samples at temperatures above 500 K. Recent temperature programmed desorption studies performed in our laboratory, which will be reported in a future publication, provide additional support for this assignment.[30] In these studies it was observed that the desorption temperature for CO from monolayer and submonolayer Pd films on ZnO(0001) decreases significantly upon annealing the samples to temperatures above 700 K. The peak shift (>50 K) is too large to be attributed to changes in the morphology of the Pd film but is consistent with Rodriguez's study of Pd and PdZn alloy films supported on Ru(001) which demonstrated that alloying Pd with Zn weakens the interaction of CO with the metal.[29]

The results obtained in this study therefore indicate that at relatively low temperatures in the moderately reducing conditions of UHV, reaction of Pd with the ZnO(0001) surface to form a PdZn alloy is facile. These results are also consistent with studies of high surface area Pd/ZnO catalysts, where relatively mild reducing conditions are needed to promote alloy formation. For example, as noted above Iwasa *et al.*[4–6] observed the formation of a PdZn alloy upon reducing a Pd/ZnO catalyst in H_2 at only 573 K. PdZn alloy formation on Pd/ZnO catalysts has also been reported by Chin *et al.* for similar conditions.[1]

V. CONCLUSION

HREELS, XPS, and LEED were used to characterize the growth and thermal stability of vapor deposited Pd films on ZnO(0001). Pd film growth at 300 K proceeded via 2DI growth, where two-dimensional Pd islands were formed up to a coverage of 0.55 ± 0.05 ML at which point additional growth occurred on top of the metal islands. Pd films grown at 300 K were only metastable and agglomerated into particles that were oriented with respect to the ZnO(0001) surface upon heating. Partial agglomeration of the Pd film was observed upon heating to only 350 K, indicating that Pd interacts only weakly with the ZnO(0001) surface. XPS results indicate that upon heating to 700 K and above the supported Pd reacts with the ZnO(0001) surface resulting in the formation of a PdZn alloy.

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[1] Y.-H. Chin, R. Dagle, J. Hu, A. C. Dohnalkova, and Y. Wang, Catal. Today **77**, 79 (2002).
[2] G. Xia, J. D. Holladay, R. A. Dagle, E. O. Jones, and Y. Wang, Chem. Eng. Technol. **28**, 515 (2005).
[3] E. S. Ranganathan, S. K. Bej, and L. T. Thompson, Appl. Catal., A **289**, 153 (2005).
[4] N. Iwasa, M. Yoshikawa, W. Nomura, and M. Arai, Appl. Catal., A **292**, 215 (2005).
[5] N. Iwasa, S. Masuda, N. Ogawa, and N. Takezawa, Appl. Catal., A **125**, 145 (1995).
[6] N. Takezawa and N. Iwasa, Catal. Today **36**, 45 (1997).
[7] N. Iwasa and N. Takezawa, Top. Catal. **22**, 215 (2003).
[8] C. T. Campbell, K. A. Daube, and J. M. White, Surf. Sci. **182**, 458 (1987).
[9] J. Yoshihara, J. M. Campbell, and C. T. Campbell, Surf. Sci. **406**, 235 (1998).
[10] G. Thornton, S. Crook, and Z. Chang, Surf. Sci. **415**, 122 (1998).
[11] W. T. Petrie and J. M. Vohs, J. Chem. Phys. **101**, 8098 (1994).
[12] P. V. Radulovic, C. S. Feigerle, and S. H. Overbury, J. Phys. Chem. B **104**, 3028 (2000).
[13] A. W. Grant, J. H. Larsen, C. A. Perez, S. Lehto, M. Schmal, and C. T. Campbell, J. Phys. Chem. B **105**, 9273 (2001).
[14] A. W. Grant, L. T. Ngo, K. Stegelman, and C. T. Campbell, J. Phys. Chem. B **107**, 1180 (2003).
[15] L. T. Ngo, L. Xu, A. W. Grant, and C. T. Campbell, J. Phys. Chem. B **107**, 1174 (2003).
[16] C. T. Campbell, Surf. Sci. Rep. **27**, 1 (1997).
[17] W. Gaebler, K. Jacobi, and W. Ranke, Surf. Sci. **75**, 355 (1978).
[18] H. Jacobs, W. Mokwa, D. Kohl, and G. Heiland, Surf. Sci. **160**, 217 (1985).
[19] S. Giorgio, H. Graoui, C. Chapon, and C. R. Henry, Mater. Sci. Eng., A **229**, 169 (1997).
[20] C. A. Leighton, A. J. Swift, and J. C. Vickerman, Surf. Sci. **253**, 220 (1991).
[21] *Handbook of X-Ray Photoelectron Spectroscopy*, edited by C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg (Perkin-Elmer, Eden Prairie, Minnesota, 1979).
[22] F. Xu, Q. Guo, and P. J. Møller, J. Phys. Chem. B **109**, 9517 (2005).
[23] Y. Goldstein, A. Many, I. Wagner, and J. Gersten, Surf. Sci. **98**, 599 (1980).
[24] A. Many, I. Wagner, A. Rosenthal, J. I. Gersten, and Y. Goldstein, Phys. Rev. Lett. **46**, 1648 (1981).
[25] H. Ibach, Phys. Rev. Lett. **24**, 1416 (1970).
[26] H. van Hove and R. Leysen, Phys. Status Solidi A **9**, 361 (1972).
[27] M. Grunze, W. Hirschwald, and D. Hofmann, J. Cryst. Growth **52**, 241 (1981).
[28] M. Burn, A. Berthet, and J. C. Bertolini, J. Electron Spectrosc. Relat. Phenom. **104**, 55 (1999).
[29] J. A. Rodriguez, J. Phys. Chem. **98**, 5758 (1994).
[30] P. Bera and J. M. Vohs (unpublished).

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