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# Structure of Au and Pt Films on Pd(110): Deposition Temperature and Coverage Dependent (1x2) and (1x3) Reconstructions

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We present the results of a LEED study of the structures of Au and Pt films grown on Pd(110). We observe both (1x2) and (1x3) overlayer structures depending upon the coverage and deposition temperature. We explain the coverage and deposition temperature dependence of these reconstructions in terms of basic factors which control film growth processes.

## 1. Introduction

The growth and structure of ultra-thin metal films is an on going topic of research in our laboratories. We have been particularly interested in the growth of metal films whose bulk surfaces are known to reconstruct, and how the factors which control film growth can affect the bulk-like reconstructions of these films. The (100) and (110) low index faces of bulk Au, Pt and Ir are known to reconstruct [1]. Many studies of the growth of Au and Pt overlayers have appeared in the literature [e.g.,2-7], however, all workers to date except Fenter and Gustafsson [8] have studied the growth of these metals on the more atomically-smooth fcc (111) and (100) crystal faces. We therefore have recently concentrated our efforts on the study of metal films on an fcc (110) substrate, Pd(110).

## 2. Experimental Results

We have measured the LEED intensity profiles for Au films as a function of coverage and annealing temperature. All data presented follow deposition at 130 K. For a coverage of 1 Au monolayer a (1x1) diffraction pattern is observed, and no fractional order spots or streaking are detected. For Au coverages greater than 1 monolayer, we observe the appearance of additional fractional order beams. These data are displayed in Fig. 1. At a coverage of 1.5 to 2.0 monolayers, Fig. 1(a) and 1(b) respectively, the Au films reconstruct irreversibly to a (1x2) at temperatures slightly above 300 K. For the 1.5 monolayer film of Fig. 1(a), the best (1x2) is observed at 530 K. For temperatures over 530 K, the half-order spots are lost and a (1x1) pattern is recovered. For the 2 monolayer film of Fig. 1(b) the half-order spots are broader for lower temperatures, but sharpen and give a good (1x2) pattern at 640 K. As the temperature is increased past 640 K the intensity of the half-order spots decrease and are finally lost after annealing to 770 K. When the Au coverage is increased further to 3 and 4 monolayers, Fig. 1(c) and 1(d) respectively, the half-order spots split continuously with increasing coverage and eventually a full (1x3) structure develops by 4 monolayers. For Au coverages in excess of 4 layers a (1x3) pattern is always observed after annealing, and follows the same evolution of superstructures with temperature as for the 3 and 4 monolayer cases.

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However, the quality of the diffraction pattern for these higher coverages degrades substantially. AES results indicate that the Au coverage begins to decrease at 530 K for all the films studied. This observation suggests dissolution of the film and thus explains the irreversibility of the (1x1) to (1x2) transition.

We have measured the LEED intensity profiles for a series of Pt films as a function of annealing temperature following deposition at 300 K. For a coverage of 1 Pt layer a (1x1) diffraction pattern is observed, and no fractional order spots or streaking are detected. As the Pt film thickness is increased to 2 monolayers heavy streaking appears. For higher Pt coverages we observe the appearance of additional fractional order beams that grow in intensity as the film is slowly annealed. These data are displayed in Fig. 2. At a coverage of 2 Pt layers, Fig. 2(a), some intensity centered around the half-order position is evident after annealing to 370-400 K, although it is very broad and is essentially featureless. Following deposition of 3 Pt layers, Fig. 2(b), the same streaking appears after annealing to 370-400 K as was observed after annealing 2 monolayers of Pt to the same temperature. Increasing the temperature further results in a splitting of the half-order spot. The two components diverge as the temperature is raised and reach third order positions at 630 K. Annealing to temperatures higher than 630 K results in complete loss of the fractional-order components. The continuous splitting of the half-order spot as the film is annealed to higher temperatures is more apparent for thicker Pt films as evident in Figs. 2(c) and 2(d). For films of this coverage the splitting and the loss of the fractional-order spots occurs at slightly higher temperatures than those found for the 3 monolayer case. AES indicates for all films that the temperature at which the half-order spot begins to split, the Pt Auger signal begins to decrease. This behavior suggests that dissolution and/or agglomeration of the Pt films is in some way associated with the spot splitting.

For the Pt films, we also observe a dependence of the evolution of the LEED superstructures with the deposition temperature as shown in Fig. 3. We find that for deposition temperatures below 200 K we can stabilize the (1x2) structure. A sharp and intense (1x2) develops upon annealing to ca. 410 K, only if the film is 3 monolayers deep and is deposited between 130 and 200 K, Figs. 3(a) and (b). If the same amount if Pt is deposited at higher substrate temperatures, 225 K, the half-order spot shows signs of splitting when annealed, Fig. 3(c). For deposition of 3 layers of Pt at 300 K, Fig. 3(d), annealing brings on the (1x3) structure. At all higher Pt coverages annealing brings on the (1x3) structure independent of the deposition conditions.

## 3. Discussion

We believe that the (1x2) and (1x3) structures for both the Au and Pt films on Pd(110) can be categorized as reconstructions of the films and is not due to the formation of an ordered alloy phase. Supportive evidence for this is discussed in more detail elsewhere [9,10]. The formation of the (1x3) by the continuous splitting of the half-order spot, to the best of our knowledge, has not been reported for reconstructions of bulk surfaces or for the reconstructions of metal films. Similar spot splitting for lattice gas systems has been explained by a statistically random distribution of (1x2) and (1x3) phases each having dimensions smaller than the coherence width of the LEED optics [11,12]. We therefore adopt a similar explanation for our results.

Although the (1x2) structure has been reported most frequently for the bulk surfaces of Au and Pt (110), (1x3) structures have also been observed. However, STM results on a Au(110) surface show that the (1x3) occurs in regions of strong disorder [13], and for studies of bulk Pt(110) the (1x3) could only be stabilized by high temperature oxygen treatments [14,15]. These studies suggest that the (1x3) is not the most stable phase, and develops due to some type of disordering of the (1x2) structure. We therefore explain the development of the (1x3) as a break down in the two-dimensional order of the films as the coverage and deposition temperature changes, resulting from factors which affect film growth processes [9,10].

We have shown that Au on Pd(110) follows a Stranski-Krastanov growth mode, with a critical film coverage of 2 layers [9]. As the Au coverage exceeds 2 layers, the two-dimensional order of the films begin to break down due to the strain induced by the 4.8% lattice mismatch. This two-dimensional disorder induced by the defective nature of the film favors the formation of the (1x3) structure. For 3 monolayers of Au both the (1x2) and areas of (1x3) coexist resulting in the half-order spot splitting. By 4 monolayers of Au the (1x3) phase is the dominant species and results in the (1x3) pattern.

A similar explanation can be used for the transition to the (1x3) in the Pt films. However, for the Pt films the break down in the two-dimensional order of the film is not induced by lattice strain but by thermodynamic factors. The surface free energy for Pt in greater than that for Pd, 2.69 $J\backslash m^2$ and 2.04 $J/m^2$ respectively [16]. These conditions may favor growth in a more three-dimensional manner leading to a break down in the two-dimensionality of the film at higher temperatures [17]. However, dissolution of the film can not be ruled out as a contributing factor. In any case, as the temperature is raised the two-dimensional quality of the film begins to deteriorate, due to agglomeration and/or dissolution, which favors the formation of the (1x3) structure. As the temperature increases the (1x3) grows at the expense of the (1x2) and at higher temperatures the (1x3) phase becomes the dominant species.

The deposition temperature dependence for the stabilization of the (1x2) may be explained by a model which consists of a combination of kinetic and thermodynamic effects which control film growth at the Pt-Pd interface [10]. As mentioned earlier, thermodynamic factors may force a break up in the two-dimensional order of the film as the temperature increases and equilibrium is approached [17]. Low temperature deposition may act to kinetically limit this transition due to a reduced adatom mobility. It is therefore possible that for deposition at 130 K the film is kinetically trapped into a smoother more continuous film. Due to the better layer-by-layer quality following low temperature deposition the long range order of the (1x2) which forms is higher, and therefore the film produced under these conditions is more stable. Deposition at higher temperatures allows diffusion of the adatoms and results in some microscopic disruption in the two-dimensional quality of the film. This disruption results from roughness induced by the film's thermodynamic drive toward three-dimensional growth. The films deposited at higher temperatures are less stable due to the reduced long range order of the (1x2), and as temperature is increased disorder increases and the (1x3) is formed.

## 4. Conclusions

We observe both (1x2) and (1x3) reconstructions for the Au and Pt on Pd(110) film systems. The (1x3) structure in both systems is found to evolve by the continuous splitting of the half-order spot. We propose for both of these systems that the transition of the (1x2) to the (1x3) results from a slow break down of the two-dimensional order of the films which favors the formation of the (1x3) structure. We believe that the main differences in the (1x2) to (1x3) transitions for these two systems lies in the thermodynamic differences for each respective metal pair, and in the different strain energies involved at the interface resulting from the dissimilar lattice mismatches.

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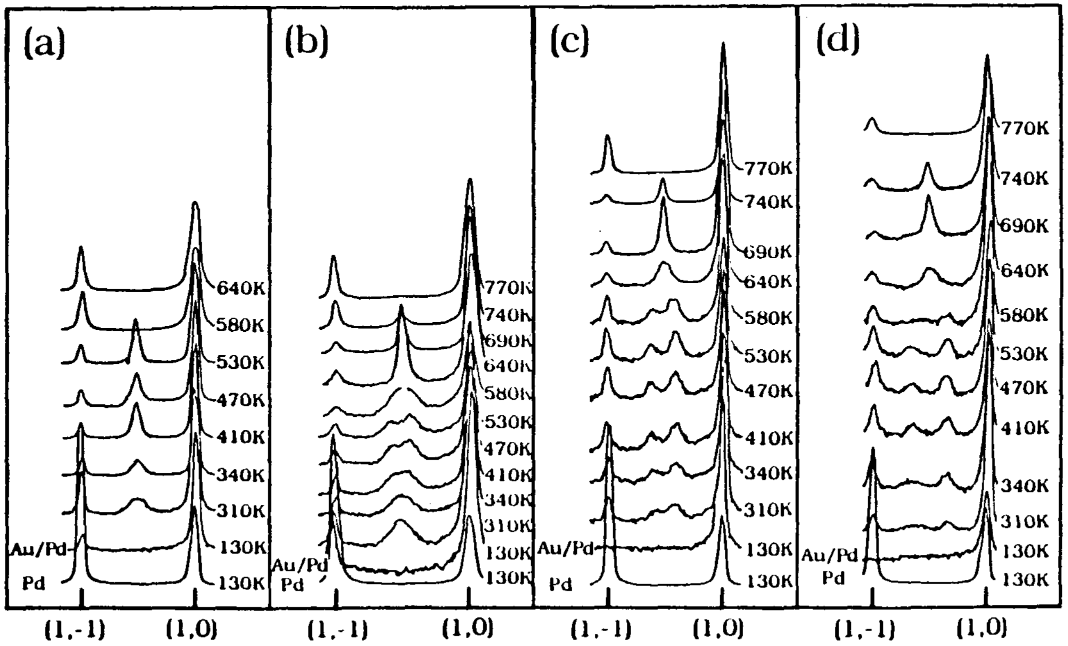
**Figure Captions:**

Figure 1. LEED intensity profiles for Au films on Pd(110) as a function of annealing temperature following deposition at 130 K. Profiles are taken along the [001] direction between the (1,0) and (1,-1) beams at a beam energy of 72 eV. Coverages shown are: a) 1.5 monolayers; b) 2 monolayers; c) 3 monolayers; and d) 4 monolayers.

Figure 2. LEED intensity profiles for Pt films deposited at 300 K as a function of annealing temperature. Profiles are taken along the [001] direction between the (0,0) and (0,-1) beams at a beam energy of 35 eV. Coverages shown are: a) 2 monolayers; b) 3 monolayers; c) 5 monolayers; and d) 15 monolayers.

Figure 3. LEED intensity profiles for 3 layer Pt films deposited between 130 and 300 K as function of annealing temperature. Profiles are taken along the [001] direction between the (0,0) and (0,-1) beams at a beam energy of 35 eV. Deposition temperatures are: a) 130 K; b) 200 K; c) 225 K; and d) 300 K.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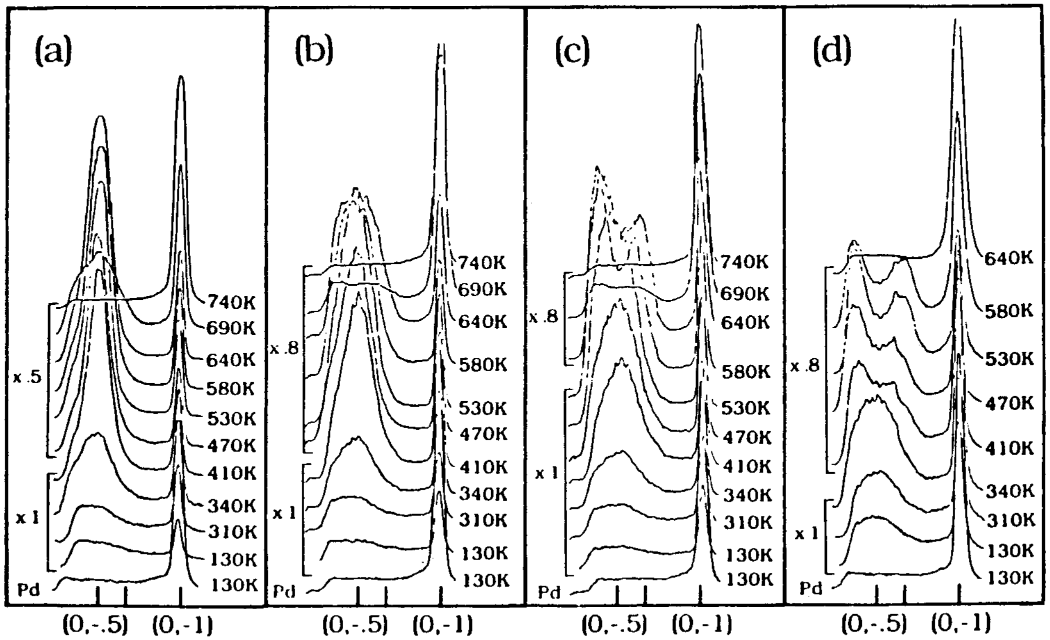
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