

On the structure and dynamics of thin Ar films on Pt(111)

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The structure and lattice dynamics of thin Ar films physisorbed on Pt(111) have been investigated using He-diffraction and inelastic He-scattering.

The He-scattering apparatus is described in detail elsewhere¹. Structural information is obtained by monitoring the total scattered He-intensity as a function of the wave-vector transfer Q parallel to the surface. The total scattering angle being fixed at $\theta_i + \theta_f = 90^\circ$, Q , is varied by rotating the sample and thereby changing both incident and outgoing angles θ_i and θ_f simultaneously. Phonon spectra are recorded by Time-of-Flight analysis of the scattered He-beam. In the experiments reported below a He-beam energy of 18.3 meV has been used, resulting in an overall wave-vector and energy resolution of $\Delta Q = 0.02 \text{ \AA}^{-1}$ and $\Delta E = 0.32 \text{ meV}$, respectively.

Ar is adsorbed on the Pt(111) surface from the 3D-gas phase at low surface temperatures ($\approx 20 \text{ K}$). The Ar coverage is readily obtained by monitoring the specularly reflected He-intensity².

Ar adsorbs on the clean Pt(111) surface in a hexagonal solid phase aligned with respect to the substrate. In the submonolayer regime a structural phase transition of the physisorbed Ar layer is observed at a coverage $\Theta \approx 0.75$ ($\Theta = 1$ referring to full monolayer coverage): At lower coverage ($\Theta < 0.6$) the first order diffraction peak of the Ar-phase is centered at $Q = 1.90 \text{ \AA}^{-1}$, corresponding to a lattice parameter $a = 3.81 \text{ \AA}$. Upon increase of the Ar coverage a second first-order diffraction peak at $Q = 1.96 \text{ \AA}^{-1}$ emerges, corresponding to an Ar-phase with lattice parameter $a = 3.70 \text{ \AA}$ i.e. slightly compressed with respect to the first. While the intensity of the first peak continuously decreases upon further Ar-adsorption, the second peak at $Q = 1.96 \text{ \AA}^{-1}$ becomes more intense. At $\Theta \approx 0.75$ the two diffraction peaks have about equal intensities while above $\Theta \gtrsim 0.9$ the first peak has vanished and only the second one is observed. The discontinuous change of the diffraction peak position and the observed phase coexistence indicate that this phase transition is of first order.

Since a discontinuous transition between two incommensurate (floating) phases as a function of coverage is not likely to occur, we have looked for commensurate structures—in particular for

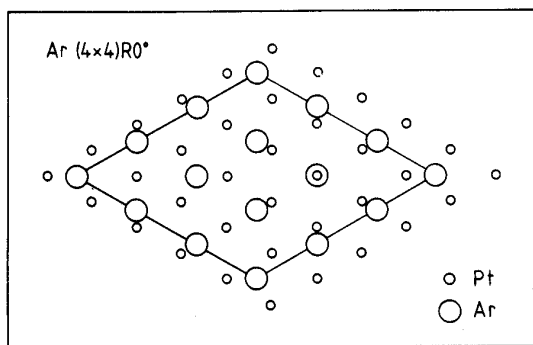


Figure 1. $(4 \times 4)R0^\circ$ high-order commensurate structure of the Ar monolayer ($\Theta \gtrsim 0.75$) on Pt(111). Small circles correspond to Pt atoms, large circles to Ar adatoms.

so called high-order commensurate (HOC) phases, which consist of a commensurate unit cell with a multiatomic basis. As shown in the case of Kr/Pt(111)² the thermal expansion of the adlayer as well as the presence of additional diffraction satellites due to the commensurate superstructure can be used as experimental criteria to distinguish between HOC and incommensurate (I) structures. These criteria have been used here to characterize the nature of the two Ar phases on Pt(111).

The Ar phase at higher coverage shows no significant thermal expansion in contrast to the large expansion of bulk Ar, indicating that the adlayer is a locked commensurate phase. In addition, superstructure peaks are observed in this high coverage phase at $1/3$ and $2/3$ of the wave-vector position of the first order Ar diffraction peak. Thus the period of the commensurate unit cell equals three interatomic Ar distances ($\sim 11 \text{ \AA}$). From the known lattice parameter of the Pt(111) substrate $a_{\text{Pt}} = 2.77 \text{ \AA}$ it follows that the Ar phase at higher coverage ($\Theta \gtrsim 0.75$) is a $(4 \times 4)R0^\circ$ HOC-phase with a commensurate unit cell of length $3 \times a_{\text{Ar}} = 4 \times a_{\text{Pt}} = 11.08 \text{ \AA}$. This is shown schematically in Figure 1.

The analysis of the low coverage phase is more difficult. Although further investigation is needed for a final conclusion, our experimental data indicate, that also the low coverage Ar phase ($\Theta \lesssim 0.75$) is partially locked. The possible HOC phases, however, have rather large unit cells ($\gtrsim 40 \text{ \AA}$) resulting in a thermally less stable and more disordered adlayer structure.

After monolayer completion Ar multilayers on Pt(111) adsorb in a layer-by-layer growth mode. This follows from He-diffraction as well as from the layer specific phonon dispersion of the multilayer Ar films. The results are quite similar to those obtained previously on thin Kr films on Pt(111)³.

In particular, a strong coupling of the adlayer modes to the Pt-substrate phonons could be observed in the Ar mono-, bi- and trilayers. As with the Kr films³ this coupling results in a hybridization of the adlayer mode with the Rayleigh wave of the Pt substrate and a linewidth broadening of the adlayer phonons due to the coupling to the projected bulk density of states of the substrate ('radiative damping')^{4,5}. In addition, however, for the first time the coupling to the longitudinal bulk band edge as predicted by theory⁴ could be observed in the Ar monolayer. Evidence for the hybridization of the adlayer mode with the longitudinal bulk band edge of the Pt substrate is obtained through an enhancement of the measured linewidth in the narrow region of the Brillouin zone ($Q = 0.3 \pm 0.1 \text{ \AA}^{-1}$) where this hybridization is expected to occur.

The fact that in the Kr monolayer this coupling could not be observed experimentally can be explained by the much larger linewidth broadening due to radiative damping in the monolayer phonons in Kr ($\sim 0.5 \text{ meV}$) as compared to Ar ($\sim 0.2 \text{ meV}$).

References

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