Two-dimensional metal gas–solid phase transition: dynamical work function measurements during Ag deposition on Ru\(^{(0001)}\)

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Abstract

A two-dimensional phase transition during deposition of Ag on Ru(0001) was found at coverages below 0.1 ML. This phase transition is investigated by work function measurements performed in-situ, i.e. during Ag deposition, with a Kelvin probe. A value for the heat of two-dimensional vaporization is obtained by an analysis based on the Clausius–Clapeyron equation and compared with lateral Ag–Ag interaction energies derived from Monte Carlo simulations of thermal desorption spectra of this heteroepitaxial system.

Keywords: Growth; Low index single crystal surfaces; Ruthenium; Silver; Surface thermodynamics; Thermal desorption spectroscopy; Work function measurements

1. Introduction

The most appropriate methods to investigate the growth of thin metal films are in-situ methods since they provide information about the growth mode \textit{during} deposition. Well known is the observation of oscillations during a layer-wise growth, e.g. by means of TEAS or RHEED (see, e.g., Refs. [1,2]). Recently we have shown that also in-situ measurements of the work function change \((\Delta \Phi)\) by means of a Kelvin probe are a suitable tool to monitor the film growth. This was demonstrated by the detection of oscillations in the work function during the growth of Cu on oxygen precovered Ru(0001) [3–5] as well as on Pt(111) [6]. Apart from this \textit{qualitative} classification of the growth-mode the present work shows that also \textit{quantitative} parameters relevant for the growth process are accessible from such in-situ work function change measurements using a so-called Pendulum–Kelvin probe.

Although the understanding of epitaxial film growth has made remarkable progress it is still difficult to predict non-equilibrium growth-structures of metal films at a certain growth temperature and deposition rate. While the equilibrium growth-mode is only determined by thermodynamics non-equilibrium growth is determined by kinetics which results in a complex situation especially in the case of heteroepitaxial growth. In the region of submonolayer coverages the atomic interaction energies of the adatoms with each other and with the substrate deter-
mine the processes of nucleation and activation barriers for diffusion and thereby the structure and morphology of the growing film.

In order to achieve a better understanding of the initial stages of thin film-growth it is therefore necessary to collect reliable quantitative data for adatom–adatom interaction energies. A comparison of experimental data with simulations, e.g. Monte Carlo simulations, of thermal desorption spectra (TDS), allows one to retrieve such atomic interaction energies. With these data other questions, e.g. about the miscibility in the case of coadsorption systems, can in principle also be answered via simulations as recently reported for the Cu/Ag/Ru(0001) system [7,8]. However, such a comparison does not reveal the interaction energies in a straightforward manner so that an independent experimental check is desirable in order to refine the microscopic models and to enhance the reliability of the theoretical predictions. This can be done by studying the thermodynamic stability of 2D adatom islands [9].

A thermodynamic quantity which is not only directly measurable but also available from Monte Carlo simulations is the heat of two-dimensional vaporization ($\Delta H_{2D}$). In the simulations it can be calculated from the interaction energies used as parameters to fit the measured TD-spectra, while experimentally this quantity can be derived from the observation of a 2D phase transition between an adatom gas and a 2D condensed phase. This has already been done with in-situ TEAS measurements [10] and via ex-situ work function measurements [11].

Using the latter, Kolaczkiewicz and Bauer have studied the phase transitions of various metal deposits on tungsten and molybdenum surfaces at constant coverages by means of the EBM (= retarding field electron beam method) technique [11–13]. These measurements were performed during cooling of the sample from high temperature after deposition of the appropriate amounts of the metals.

Here we want to show that the heat of 2D vaporization can also be derived from in-situ $\Delta \Phi$-measurements, i.e. the phase transition of a 2D gas to a 2D gas + 2D condensed phase of Ag on Ru(0001) is followed during metal deposition at different substrate temperatures. The experimental results are compared with microscopic parameters such as lateral interaction energies used in the above mentioned simulations of TD spectra of the Ag/Ru(0001) system.

2. Experimental

As already mentioned the experiments were carried out by means of a special Pendulum–Kelvin probe [14] which uses a reference electrode vibrating parallel to the sample surface. The advantage of such a device is that the work function changes can be monitored in-situ, i.e. during metal deposition, with an accuracy of 2 meV. Details of the experimental set-up are described elsewhere [5]. The preparation of the Ru substrate followed standard procedures and was checked by AES. The miscut of the crystal is less than 0.5°, the step density less than 1%. Ag was evaporated from a resistively heated tungsten basket at a low background pressure of $3 \times 10^{-10}$ mbar. The work function change is measured as a function of deposition time. The latter was controlled by a mechanical shutter while the deposition rate was held constant. The absolute coverage was calibrated by means of additional Ag-TDS experiments with films deposited with the same deposition rate. This is possible within an accuracy of 5%, taking advantage of the clear separation between the first monolayer and the second layer Ag-desorption-peaks [15]. 1 ML Ag is defined as the amount necessary for completion of the first slightly strained Ag layer on the hexagonal Ru(0001) surface [16].

3. Results

Fig. 1 shows the work function change ($\Delta \Phi$) obtained during Ag deposition on the Ru(0001) surface in the submonolayer coverage regime for two different substrate temperatures (350 and 890 K). While curve 1 registered at a deposition temperature ($T_d$) of 350 K shows a monotonic, almost linear decrease of $\Phi$, the shape of curve 2 taken at $T_d = 890$ K initially shows a much stronger work function decrease up to a coverage of $\sim 0.06$ ML. Upon further Ag deposition a distinct knee in the slope is followed by a slower linear decrease of $\Phi$.

The steeper work function decrease at 890 K can be explained in terms of the existence of a two-di-
Fig. 1. Work function change (ΔΦ) upon Ag deposition (start indicated by the arrow) on a Ru(0001) surface at two different substrate temperatures as a function of Ag coverage (deposition rate R = 0.36 ML/min). At 350 K a linear ΔΦ decrease is observed corresponding to growth of 2D islands (curve 1). At 890 K (curve 2) two linear ΔΦ segments can be distinguished in the submonolayer regime, the first steep one indicating the existence of a Ag 2D gas phase. The coverage calibration is performed using Ag TD-spectra (see text).

Fig. 2. Work function change during Ag deposition at various substrate temperatures and constant deposition rate (R = 0.36 ML/min). The 2D gas-condensed phase transition is observed in the low coverage regime (Θ = 0.02–0.06 ML). The intersection of the extrapolated linear ΔΦ segments (dotted lines) yields the onset of 2D condensation.

Fig. 3. Work function change of a Ru(0001) surface covered with 0.1 ML Ag at 400 K upon annealing from 400 to 900 K (heating rate 1 K/s). The ΔΦ decrease is due to the transition of Ag adatoms from the condensed islands into a 2D gas. Cooling of this "surface vapor" results in a ΔΦ increase of the same height showing the reversibility of the phase transition (cooling rate between ~11 K/s and 1.3 K/s). This experimental behavior could be reproduced several times without changes in the shapes of the ΔΦ curves.
that in all curves the initial decrease follows the same line up to the respective saturation coverage $\Theta_{sat}$. A complementary experiment is shown in Fig. 3. After deposition of $\sim 0.1$ ML Ag at $T_d = 400$ K the $\Delta \Phi$-change was recorded at this given Ag coverage as a function of temperature like in the work of Kolaczkiewicz and Bauer [11]. In the main frame of the figure it can be seen, that the work function decreases by $\sim 0.15$ eV with increasing temperature. The heating rate was 1 K/s. The inset shows that this process is completely reversible when the sample is cooled to 400 K, although the cooling was not linear in time and much faster (cooling rate varies between $\sim 11$ K/s and $\sim 1.3$ K/s) than the annealing procedure. It is important to note here, that this large and reversible change of the work function is unambiguously due to changes within the adsorbed Ag layer, since the clean substrate showed only very minor changes ($< 0.02$ eV) of $\Phi$ during the same annealing procedure as proven by separate measurements. Furthermore Ag does not form an alloy with the Ru substrate [16,18].

The fact that this reversibility is independent of the large difference between heating- and cooling-rate, indicates that the conditions of thermodynamical equilibrium are fulfilled during the presented measurements. In Fig. 4 a work function measurement is shown which was to monitor the influence of different deposition rates on the onset of condensation at constant substrate temperature. Even though the deposition rates differ by a factor of $\sim 2.5$ the comparison between curve 2 and the rescaled curve 1 (dotted line) shows that this variation of the deposition rate does not affect the 2D condensation process on the surface. In view of the employed method of analysis for the measured phase transition, this is another important experimental finding besides the reversibility shown in Fig. 3, and will be addressed again in the following discussion.

4. Discussion

In this section we analyse the measured $\Delta \Phi$-data in terms of the two-dimensional heat of vaporization $\Delta H_{2D}$ of the silver deposit on Ru(0001). The analysis of the data is based on an equation of the Clausius–Clapeyron type for the phase transition 2D gas $\leftrightarrow$ 2D condensate. The application of the Clausius–Clapeyron equation in the study of two-dimensional phase transitions has been demonstrated earlier for such different systems as noble gas atoms or metal adatoms on single crystal surfaces [10,11]. Since the general theoretical basis of the analysis is the same as in the work function studies mentioned before, we will put more emphasis on the discussion of the prerequisites of the analysis which have to be fulfilled, i.e. equilibrium conditions between gas and condensate during Ag deposition in the very low coverage regime. This will be followed by a discussion of several microscopic processes possibly influencing the determination of $\Delta H_{2D}$. Finally, as mentioned in the introduction, the extraction of a value for the Ag–Ag interaction energy from the thermodynamic quantity $\Delta H_{2D}$ is compared with that obtained from detailed Monte Carlo simulations of Ag TD-spectra from Ru(0001).

If the 2D gas consists of single adatoms in the temperature regime under investigation and neglecting the (usually rather small [11,19]) temperature dependence of the mean dipole moment $\mu$ per Ag adatom in the gas phase, the atomic density $n$ of the gas phase is obtained by the well-known Helmholtz-equation [20]:

$$\Delta \Phi = -4 \pi e n \mu.$$  

(1)
With the gas phase approximated by a perfect 2D gas at coverages below the phase transition the equilibrium spreading pressure $\Pi$ of the gas phase ($\Pi = \frac{RT}{n}$) is proportional to the measured work function change:

$$\Pi = \text{const} \cdot \Delta \Phi T.$$  

(2)

In the coverage regime of the phase transition the area covered by the condensate may be neglected compared to the the area $A = \frac{1}{n}$ covered by the 2D vapor phase. The temperature dependence of $\Pi$ is then determined by a 2D Clausius–Clapeyron equation of the following form:

$$\left(\frac{d \Pi}{dT}\right)_{\text{Kex}} = \frac{\Delta H_{2D}}{TA},$$  

(3)

$\Delta H_{2D}$ being the heat of 2D vaporization. Combining Eqs. (1)–(3) and integrating leads to

$$\ln \Delta \Phi + T = -\frac{\Delta H_{2D}}{RT} + \text{const.}$$  

(4)

A plot of $(\ln \Delta \Phi + \ln T)$ versus $1/T$ yields a straight line if the assumptions leading to Eq. (4) are fulfilled under the experimental conditions, and the slope is proportional to $\Delta H_{2D}$. Using the intersection point of the two straight lines fitted to curves as depicted in Fig. 2 (as exemplified for the 890 K curve) as a measure of the saturation coverage of the 2D vapor phase at the given temperature we have constructed the $(\ln \Delta \Phi + \ln T)$ versus $1/T$ plot shown in Fig. 5. The data fall remarkably well onto a straight line the slope of which yields a value of $0.33 \pm 0.02$ eV/atom for the heat of vaporization of Ag islands on Ru(0001). This result may be converted into a lateral interaction energy between two sixfold coordinated Ag adatoms of $E_{\text{AA}} = \frac{1}{3} \Delta H_{2D} = 0.11 \pm 0.02$ eV.

Fig. 5. Plot of $(\ln \Delta \Phi + \ln T)$ versus $1/T$ at the 2D gas–solid transition (knees in Fig. 2) yields a straight line, the slope of which gives the 2D heat of vaporization. Further explanations see text.

Ag gas pressure, and will the 2D gas phase not be oversaturated due to impinging atoms. The validity of this condition can be verified from Fig. 4 as already described in the preceding section. The observed independence of the 2D gas phase saturation density (knee) from the deposition rate proves the instantaneous equilibration between the 2D phases on the time scale set by the deposition rate.

A proof of the state of equilibrium between the 2D phases is the reversibility of the temperature-induced work function changes as shown in Fig. 3. The shape of the curves is determined by the 2D evaporation (respectively condensation) of Ag atoms within the region of coexistence of 2D gas and condensate. This condition is met for the coverage of $\sim 0.1$ ML in Fig. 3, which exceeds the saturation coverage of the pure 2D gas phase at 890 K determined from Fig. 2 to be $\sim 0.06$ ML. This finding agrees well with earlier results [11]. In a supplementary experiment at 890 K (not shown here), the Ag flux was interrupted at a coverage below the phase transition were only the 2D gas exists, and the work function was followed with time at constant substrate temperature. No further change could be detected within the sensitivity range of the method. This further supports the reversibility of the temperature induced work function change between 400 and 900 K and again justifies the assumption of equilibrium between the 2D phases on the surface.
The formal description of the 2D Ag gas phase as a 2D perfect gas is obviously confirmed by the linear correlation between \( \ln \Delta \Phi + \ln T \) and \( 1/T \) in Fig. 5. Despite the fundamental differences of physisorbed and chemisorbed two-dimensional systems Poelssema et al. observed a similar dependence for the 2D phase transition of Xe on Pt(111) [10].

Another condition for the applicability of the Clausius–Clapeyron analysis is the temperature independence of the dipole moments in the 2D gas and condensed phase. This is well supported by the data shown in Fig. 2. The same slope and the linear initial decrease indicates the temperature and coverage independence of the dipole moment per 2D gas atom (not too close to 2D gas phase saturation).

A possible effect which could influence the value of \( \Delta H_{2D} \) is a composition of the 2D gas phase other than that of an ideal gas consisting only of monomers. Recently the coexistence of a Ag 2D gas/solid phase on Pt(111) at temperatures above 400 K and below 600 K and coverages up to 0.6 ML was reported [21]. The STM results indicate the presence of a “real” 2D gas consisting not only of single atoms but also of small Ag-clusters. However, since our measurements were done at much higher temperatures as well as lower coverages it seems reasonable to exclude the existence of adatom clusters in the 2D gas. This is in agreement with the detailed work by Kolaćzkiewicz and Bauer who also ruled out the existence of dimers at very low coverages and high temperatures on the basis of their work function measurements (see, e.g., Refs. [11,13]).

At the low coverages of the phase transition preferential nucleation at substrate steps could influence the 2D equilibrium. Due to the high substrate temperatures probably most of the diffusing adatoms could reach substrate steps. The condensation energy of a chain of Ag atoms at Ru steps could influence the measured \( \Delta H_{2D} \) value. However, as mentioned before in the experimental section the step density was estimated to be below 1%. Even the smallest saturation coverage of the Ag gas phase at 640 K (\( \sim 0.025 \) ML) exceeds the estimated number of step sites by a factor of more than 2. Since Ag atoms trapped at substrate steps should exhibit another dipole moment a change in \( (d\Delta \Phi/d\Theta) \) should be observable if the very initial nucleation at steps provides a sink for a significant amount of arriving adatoms. The same slope of \( \Delta \Phi \) versus coverage with increasing temperature (Fig. 2) as well as the strict linearity of the \( \ln \Delta \Phi + \ln T \) and \( 1/T \) plot (Fig. 5) suggest that this is not the case. Thus, the data are representative for Ag condensation mainly at Ag step sites.

Structural changes within the condensed layer (e.g. step roughening or wetting–non-wetting transitions [11,13,22]) could also influence the \( \Delta H_{2D} \) value. Again, the strictly linear dependence in the \( \ln \Delta \Phi + \ln T \) versus \( 1/T \) plot in Fig. 5 gives no indication that such transitions play any significant role in the investigated temperature range.

Finally the present result for \( \Delta H_{2D} \) as obtained from work function change measurements shall be compared with the findings from earlier Monte Carlo simulations of experimental Ag TD-spectra from Ru(0001) [7,8]. Fig. 6a displays a series of Ag TD-spectra for different initial Ag coverages, the highest spectrum corresponds to one monolayer [8]. Besides the overall temperature range of desorption a simple visual inspection of the desorption traces reveals two characteristic features.

The curves for the lowest coverages are rather symmetric in shape suggesting first order desorption kinetics. By contrast, with increasing coverage the curves turn into an asymmetric peak with a common
exponential rise, a coverage dependent shift of the maximum to higher temperature and a rather steep high temperature fall-off, which suggests a change to zeroth order desorption kinetics. The zeroth order desorption behavior is also known from other metal/metal systems and is generally explained in terms of a phase equilibrium between two coexisting phases, namely 2D gas and 2D condensed phase [23]. However, a crossing of the phase boundary during a desorption experiment may not be visible in the spectra because it occurs in the steep high temperature (low coverage) part of the spectrum. Only for very low coverages during desorption the coverage/temperature trajectory may remain in the 2D gas phase region resulting in a first order desorption behavior (see Fig. 6a).

Generally, a more quantitative analysis of thermal desorption spectra is performed in terms of a rate equation, which at best may yield average values for the preexponential factor \( \nu \), the kinetic order and the activation energy \( E_d \) of the desorption process [24]. In an earlier attempt the experimental Ag TD-spectra shown in Fig. 6a were therefore simulated using Monte Carlo methods in order to achieve a more microscopic insight in the underlying desorption process. The simulations were based on a lattice gas model using the interaction energies \( E_s \) between the substrate and a Ag adatom, and \( E_{AgAg} \) between Ag adatoms as parameters. While \( E_s \) was taken to be coverage-independent, the lateral interaction energy \( E_{AgAg} \) was chosen to depend on the coordination number \( m \) of the interacting Ag adatoms. This non-simple additivity of lateral interaction energies was first introduced by Milchev [25] and includes interactions beyond the first shell. A typical simulation run of a TD-spectrum consisted of an “equilibration run” followed by a “desorption run”. During the equilibration run the equilibrium configuration on the surface as a function of the chosen coverage and the above defined interaction parameters was established. During the desorption run the temperature was increased in steps of \( \Delta T \) and atoms were allowed to desorb with a probability \( P_d = (0, 1) \) which depends on the activation energy of desorption \( E_d = E_s + \sum E_{AgAg} \). After each successive temperature rise \( \Delta T \) the surface was reequilibrated before the next atoms were desorbed. This procedure was repeated until the coverage dropped to zero [26]. Particular emphasis in these simulations was placed on a reproduction of the spectral change in the experimental curves from first to zeroth order desorption characteristics with increasing coverage. From the best fit between simulated and experimental desorption curves (see Figs. 6a and 6b) the following two energy parameters were obtained: \( E_s = 2.65 - 2.70 \) eV/atom, and \( E_{AgAg} = 0.07 - 0.09 \) eV, the latter referring to the lateral interaction energy between two fully (six-fold) coordinated Ag adatoms.

Besides the qualitative finding with both the work function change measurements and the experimental as well as simulated TD-Spectra, i.e. the observation of a 2D gas phase at elevated substrate temperature, both described approaches yield though not exactly the same but a rather similar result for the microscopic parameter \( E_{AgAg} \). On the other hand, only a rather crude estimation of the interaction energies is available from a “complete” analytical evaluation of Ag TD-spectra as done by Niemantsverdriet et al. [27]. If the shift in the thus estimated desorption energies from low to high coverages are correlated with the two-dimensional heat of vaporization a value of \( \sim 0.17 \pm 0.04 \) eV is obtained. This value, in turn, fed into the Monte Carlo calculations yields unacceptable simulated TD-spectra.

5. Conclusions

In the present work it could be shown that in-situ work function measurements using a Kelvin probe provide quantitative data of adatom interactions for heteroepitaxial metal systems. Based on a simple Clausius–Clapeyron analysis of the work function changes measured during Ag deposition on Ru(0001) at very low coverages, a value for the heat of two-dimensional vaporization of \( 0.33 \pm 0.02 \) eV/atom is obtained. With additional experiments it was established that the condition of equilibrium – a prerequisite for the Clausius–Clapeyron analysis – is met even during the deposition process. Therefore, we believe that the present analysis provides a reliable approach to determine lateral interaction energies between adatoms. Even though the present results compare reasonably well with lateral interaction energies extracted from Monte Carlo simulations of TD-spectra of the same Ag/Ru(0001) system we
believe, however, that the values obtained from the Clausius–Clapeyron analysis are more reliable. In fact, the latter ones should be fed into the simulations (in particular, since the lateral interaction energies are not the only fit parameters in the simulations) in order to calculate other properties of the system, e.g. growth structures or phase diagrams.

References

[26] For details of the simulational scheme, see Ref. [8].