Formation of Regular Surface-Supported Mesostructures with Periodicity Controlled by Chemical Reaction Rate

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We report a LEEM and XPEEM study of the formation of a variety of stationary two-dimensional metallic and oxygen structures in Au and Au + Pd adlayers on Rh(110) during water formation reaction. They result from chemically frozen spinodal decomposition and are created, preserved, or reversibly modified by tuning the reaction conditions. The wavelength of lamellar structures obtained at intermediate metal coverage is found to obey a power scaling law with respect to the reaction rate.

Homogeneous multicomponent systems far from thermodynamic equilibrium can undergo spontaneous phase separation to reduce the total free energy of the system. This process, known as spinodal decomposition, is accompanied by development and evolution of spatial periodic structures. Generally, the characteristic length scale of such structures increases with time until macroscopic phase separation is attained.[1,2] By quenching the temporal evolution at a given stage, structures with different length scales can be created. The effects of spinodal decomposition have been extensively investigated for binary mixtures,[3] metastable liquids,[4] and thin-film growth.[5−7] The factors that govern the phase separation and control the length scale of the resulting two- or three-dimensional structures are specific for each system, e.g., the fine interplay between mobility, dipole or chemical interactions, concentration fluctuations, lattice strain, and so forth.[1,2,8]

For chemically reacting systems, spinodal decomposition as a mechanism for structure formation was first suggested in theoretical studies of polymer mixtures.[9,10] It was shown that nonequilibrium chemical reactions interconverting two separating species lead to periodic stationary structures, which were used to fabricate polymer blends with desired morphologies.[11,12] It has also been predicted that adsorbates on metal surfaces under reaction conditions can spontaneously reorganize into stationary or traveling periodic nonequilibrium nanostructures.[13−15] These phenomena, described as "chemical freezing" of phase separation, persist only in the presence of a chemical reaction and can be controlled by varying the reaction conditions. An important general theoretical prediction for various types of reactive phase-separating systems is that the characteristic wavelength of periodic structures decreases with the reaction rate following a power scaling law.[9,14−16] So far, such dependence has been observed only for a narrow parameter range in photoinduced reactions in polymer mixtures.[17]

Stationary structures resulting from reactive phase separation driven by pure energetic factors were recently observed for metal adlayers on Rh surfaces.[18−21] These studies demonstrated the prominent role of surface reactions in steering the lateral reorganization of the adspecies. However, the dependence of the morphology of the resulting structures on the reaction rate has not been considered so far. This important issue is addressed in the present study of nonequilibrium reaction-induced formation of regular structures in Au and Au + Pd films on the Rh-(110) surface. The wavelength of these structures is found to obey a power law over more than two decades of the reactants pressure.

We have studied lateral reorganization of submonolayer Au and Au + Pd films on the Rh(110) surface during the water formation reaction, employing different reaction conditions. In this system, H_2 and O_2 molecules dissociate on the Rh surface, and H and O adspecies react to form water, which immediately leaves the surface.[22] Stationary metallic structures develop at the transition from reduction to oxidation conditions. Au does not participate in the reaction but acts as an inhibitor, blocking active sites on the surface. Ab initio calculations[21] have shown that the mixed Au−O coadsorption state has a higher total binding energy than the separated gold and oxygen phases. In the more complex case of Au + Pd/Rh, phase separation into mixed AuPd and O islands is favored, because the enthalpy of formation of binary AuRh, RhPd, and AuPd alloys is negative only for the AuPd couple[23] and oxygen adatoms bind most strongly to the bare Rh surface. Although phase separation of Au (Au + Pd) and oxygen on the Rh(110) surface is energetically favored, it is kinetically hindered in the absence of chemical reaction by the very low mobility of metal and oxygen adatoms in the mixed layer. The water formation reaction dynamically removes the O adatoms from the surface, leaving empty sites which can be occupied by Au or Pd.

The interface was characterized using microscopic methods combining structural and chemical sensitivity. Low energy electron microscopy (LEEM)[24] was used to follow the formation of the adlayer structures in real time, with atomic depth resolution and lateral resolution of ∼10 nm. The local composition of the structures was determined by X-ray photoemission electron microscopy (XPEEM).[25] The initial uniform state was

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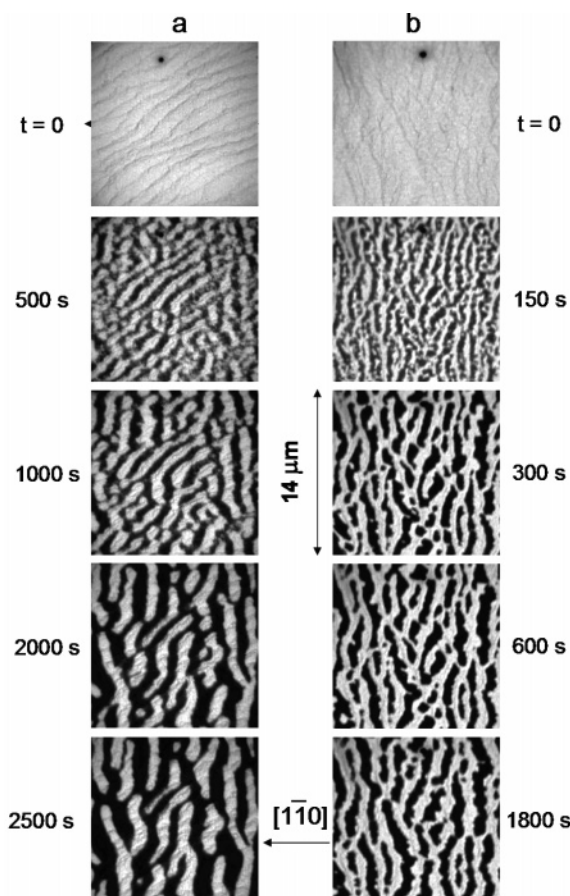
Figure 1. Development of Au structures (bright) on a Rh(110) surface, in the case of (a) $\Theta_{Au} = 0.55$ ML and (b) $\Theta_{Au+Pd} = 0.75$ ML. LEEM images from top to bottom are taken at indicated reaction times. Reaction parameters: (a) reactant pressure $p = 5.3\cdot10^{-7}$ mbar; $P[H_2]/P[O_2] = 0.5$; $T = 780$ K; (b) $p = 1.3\cdot10^{-6}$ mbar; $P[H_2]/P[O_2] = 0.8$; $T = 820$ K.
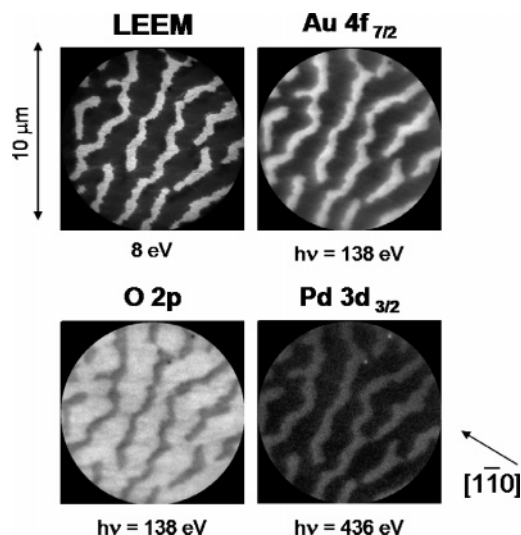

Figure 2. Morphology (LEEM) of the lamellar structure formed in a mixed Au + Pd adlayer and the corresponding elemental XPEEM images. The bright areas in the XPEEM images contain Au, Pd, and O. Metal coverage, $\Theta_{Au+Pd} = 0.5$ ML. Reaction parameters: reactant pressure $p = 5.3\cdot10^{-7}$ mbar; $P[H_2]/P[O_2] = 0.5$; $T = 820$ K. Electron and photon energies are indicated below each image.

prepared depositing Au and Pd on an atomically clean Rh(110) surface at temperatures of ~550 K.

The LEEM images in Figure 1 show the reaction-induced evolution in the morphology of (a) 0.55 monolayer (ML)[26] Au and (b) 0.75 ML Au + Pd deposited on a Rh(110) surface. Before introducing H_2 and O_2 reactants in the gas phase, the metal adatoms are uniformly distributed, and only the step bunches of the Rh surface are seen ($t = 0$ s). Due to the bistable behavior of the $O_2 + H_2$ reaction on Rh, pattern formation occurs only for a certain pressure ratio of the reactants, which depends on the coverage of adspecies. When the reaction starts, metal adatoms nucleate at the step edges. Later on, lamellar metallic arrays (bright) of increasing wavelength develop until a stationary state is reached. They tend to align normal to the [1$\bar{1}$0] crystallographic direction of the substrate. The last two images in Figure 1a,b demonstrate that at this stage of the reaction the phase separation is "frozen", i.e., the patterns become stationary. The process is reversible only when reduction conditions are imposed. In this case, the concentration of the adatoms is homogenized in few minutes.

The local composition of the structures was probed by imaging the Au 4f$_{7/2}$, Pd 3d$_{3/2}$ and O 2p core-level emission using XPEEM. Figure 2 shows that the lamellar structure consists of two alternating phases: bright regions in LEEM correspond to metallic islands on the (1 × 1) unreconstructed surface, and dark regions correspond to the oxygen adlayer, which has locally induced a (1 × n) missing-row reconstruction

of the substrate,[27] confirmed by microspot low energy electron diffraction measurements (μ-LEED) and dark-field LEEM. The local Au or Au + Pd coverage in the stationary islands is 1 ML. Depending on the reaction conditions, the oxygen-covered regions may contain a very small amount of metal adatoms.

Figure 3 illustrates how the morphology and length scales of the structures depend on reaction temperature, T, and metal coverage, Θ. The boundaries between adjacent phases are not sharp, and the dashed lines serve as guidelines. Below $\Theta = 0.3$ ML, stationary structures are not observed. For 550 K < T < 760 K and 0.3 ML < Θ < 0.75 ML, round metal islands surrounded by oxygen-covered areas develop. The fraction of the surface occupied by monolayer metal islands increases with coverage, and beyond $\Theta = 0.75$ ML, round oxygen islands (holes) inside the metal-covered surface are formed instead. At higher temperature (760–860 K), the wavelength of the structures decreases. Smaller metal islands are observed for 0.3 ML < Θ < 0.45 ML. For 0.45 ML < Θ < 0.75 ML, lamellae oriented perpendicular to the fast diffusion [1$\bar{1}$0] direction of the substrate develop. At coverage of ≥0.75 ML, holes start to develop along with lamellae. When the temperature exceeds 860 K, lamellae dissolve, and metal adatoms microscopically rearrange, decorating substrate steps and step-bunches. During reaction, the large two-dimensional metal islands observed at ~700 K (Figure 3a) can be transformed into lamellae by simply increasing the reaction temperature to 820 K. LEEM movies revealed that the islands slowly dissolve and convert into lamellar concentration patterns. This transition is reversible, i.e., the lamellae transform back to large islands when decreasing the temperature.

The phase diagram in Figure 3 has an apparent similarity to the classical phase diagram of a binary mixture, with lamellae formed in the spinodal decomposition region and islands or holes in the area where critical nucleation occurs.[9] In our case, the lamellar structure and the islands are, however, stationary and do not represent just transients, as in the classical process of Ostwald ripening. Once formed, these structures can be preserved if the sample temperature is quenched to 300 K and the reaction is ceased. Their stability was confirmed by ex situ AFM measurements.
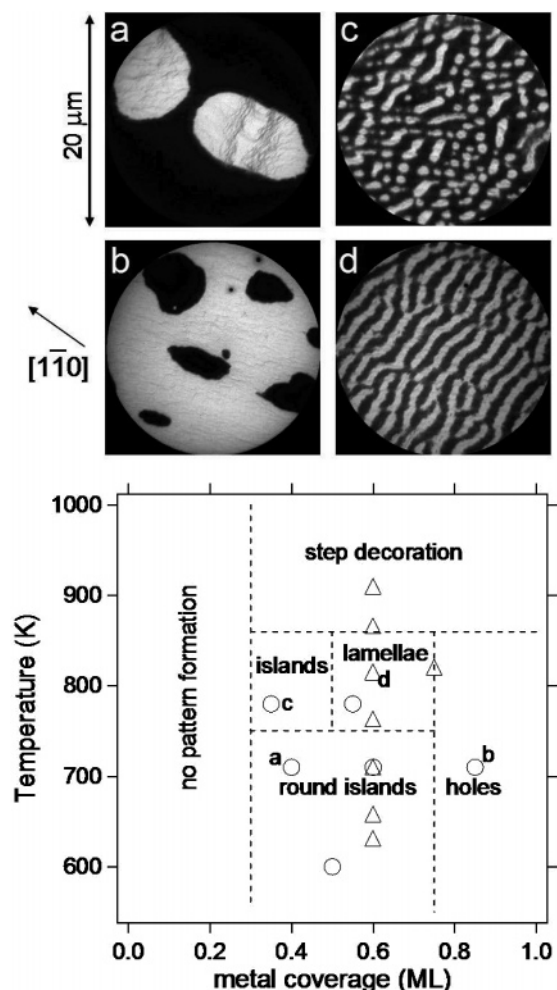
Figure 3. Shape and lateral size dependence of the stationary structures on the reaction temperature and metal coverage. LEEM images of selected structures (top) and phase diagram (bottom). The circles are for pure Au adlayers, and triangles are for Au + Pd mixed adlayers. LEEM images correspond to selected points (a−d).

Figure 4. (top) LEEM images of stationary structures formed at different gas pressures of the reactants. Metal coverage: $\Theta_{Au+Pd} = 0.75$ ML. Reaction conditions: $T = 820$ K; $P[H_2]/P[O_2] = 0.8$. (bottom) Log−log plot of the structures wavenumber along $[1\bar{1}0]$ direction vs reactants pressure. The continuous line represents the best fit to power law, with an exponent of 0.18 ± 0.02.

To investigate the influence of the reaction rate on the morphology of the stationary structures, we measured the microstructure wavelength as a function of the reactant pressures, maintaining constant temperature, metal coverage, and H_2/O_2 pressure ratio. We performed these studies for metal adatom coverage and temperature favoring formation of lamellae. In all experiments, the stationary state of the structure morphology was reached in less than 30 min. As shown in the LEEM images in Figure 4 (top), the characteristic wavelength of lamellar structures decreases with increasing reactant pressures and, hence, reaction rate. At pressures above $9 \cdot 10^{-6}$ mbar, the lamellae disappear and are replaced by large metal islands, indicating that these reaction conditions favor macroscopic phase separation. The characteristic wavenumber of the lamellae was determined by Fourier analysis of the LEEM images. As seen in Figure 4 (bottom), the dependence of the wavenumber (proportional to the inverse wavelength) on the reactant pressure follows a power law. The best fit gives a value of 0.18 ± 0.02 for the exponent. This value is very close to the exponent of 0.2 found in the experimental study of spinodal decomposition in binary polymer blends driven by photoisomerization, obeying the same power-law dependence.[17]

Detailed theoretical modeling of the system studied here is still absent. However, effects of chemical reactions on adsorbates with phase separation were analy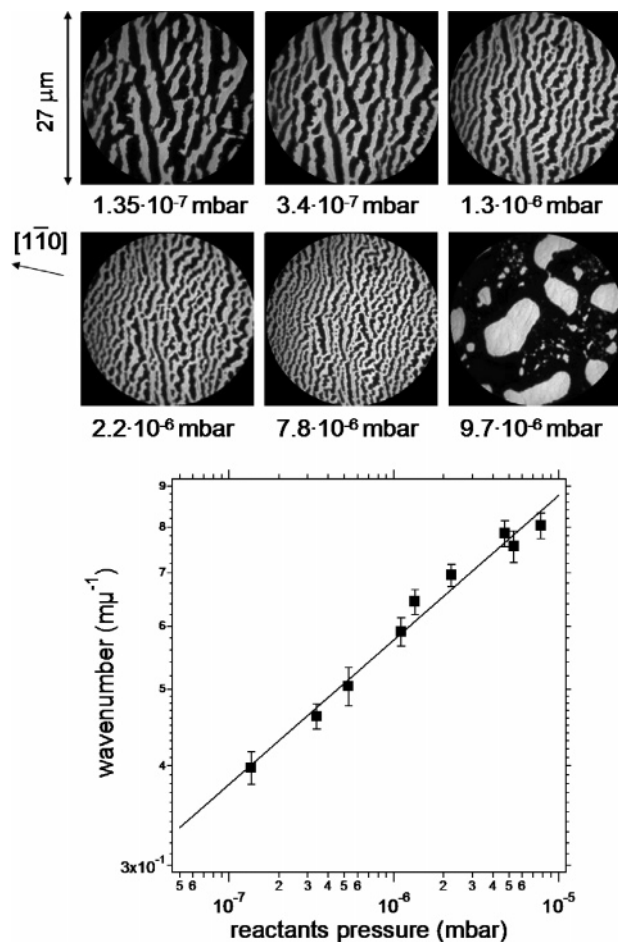tically investigated for several simple models. They included a surface chemical reaction in a monoadsorbate system with attractive interactions between adatoms, where stationary periodic lamellar structures were found,[14] and a bimolecular reaction in a two-component system, where traveling lamellae were possible.[15] Moreover, a simple model of a bimolecular surface reaction in the presence of a coadsorbed species, which has strong attractive interactions with one of the reacting species, was recently investigated.[16] While dealing with different model systems, these studies have common general predictions. In all cases, the instability boundaries of the reaction system are effectively the same as that for spinodal decomposition in absence of a reaction. The characteristic wavelength λ of nonequilibrium stationary or traveling lamellae is approximately given by $\lambda \approx \sqrt{r_0 \cdot L_{dif}}$ where r_0 is the radius of energetic interactions, responsible for phase separation, and L_{dif} is the diffusion length. $L_{dif} = \sqrt{D/k_r}$, where D is the diffusion constant and k_r is the reaction rate (thus, L_{dif} is the characteristic distance passed by an adsorbed molecule until it undergoes a reaction event leading to its disappearance). For bimolecular surface reactions at constant temperature, k_r is proportional to the reactant pressure p. Hence, the characteristic wavelength of the lamellar structures should depend on the reactant pressure as $\lambda \approx p^{-1/4}$, yielding for the wavenumber $k = 1/\lambda$, the power-law dependence with the exponent $1/4$. This is comparable to the exponent 0.18 ± 0.02 experimentally determined in our study.

Letters

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In conclusion, our findings provide new insights into the structure formation based on the phenomenon of reactive phase separation in surface reactions. This inherently nonequilibrium self-organization process is governed by the competition between kinetics and thermodynamics and can be controlled by selecting appropriate chemical reactions and by varying the reaction conditions and the coverage of the self-assembling species. We envisage that our results open a possibility for creating surface-supported microstructured functional materials with adaptable morphology.

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