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Self-organization of Ge tetramers on Ag(0 0 1) surface: A 2D realization of unusual substrate mediated interactions

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Abstract

Scanning tunneling microscopy (STM) images recorded during dissolution of a half-monolayer Ge on a Ag(0 0 1) show that it proceeds by the disappearance of tetramer entities. Moreover, they reveal that the successive slowing down in the kinetics, observed during this dissolution, correspond to the formation of ordered 2D arrangements of tetramer vacancies. A lattice gas analysis of the latter predicts a very unusual sequence of pair interactions between these vacancies, probably mediated by the substrate.

Keywords: Ising models; Construction and use of effective interatomic interactions; Scanning tunneling microscopy; Diffusion and migration; Surface structure, morphology, roughness, and topography; Surface thermodynamics; Self-assembly; Germanium

1. Introduction

The temperature dependence of the morphology and kinetics of ultra thin films deposited on metallic substrates is still the subject of many investigations in relation to the formation of surface alloys which generally present specific and original chemical and/or physical properties [1]. Generally, the main parameters which drive the thermal behaviour of the deposited element are the chemical interactions between the adsorbate and the substrate elements and their respective tendency to segregate or not at the surface of the corresponding alloy [2]. Thus, although a complete dissolution of the deposited element into the substrate is expected at sufficiently high temperature, one can observe at intermediate temperatures some blocking of the dissolution process on metastable confined phases, the so-called surface alloys [3]. In the case of the latter, it has been shown that the dissolution kinetics is governed by a local equilibrium between the surface and its selvedge [3,4] and that it is related to both its chemical composition and the atomic structure [5], with a slowing down being the signature of the formation of a surface alloy. Recently such a behaviour has been observed during the dissolution of one monolayer (ML) of Ge deposited on Ag(0 0 1) [6]. Using Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) for 1 ML of Ge in the temperature range 250–320 °C, Oughaddou et al. [6] find that kinetics always show a first part corresponding to a rapid dissolution in the bulk followed by a strong slowing down to a plateau with a concentration that depends on the temperature: at 250 °C the plateau corresponds to about 0.5 ML with a $p(2\sqrt{2} \times 4\sqrt{2})R45^\circ$ surface superstructure (which has been characterized elsewhere [7]) while at 264 °C the kinetics stops on a second plateau (which corresponds to about 0.3 ML) but surprisingly without any surface superstructure present in LEED. Since a slowing down of the kinetics is generally the signature of the formation of a specific structure, an investigation of this dissolution process using scanning tunneling microscopy (STM) is necessary to shed

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light on the nanoscopic mechanisms behind surface alloys formation and stability. This STM study is the subject of the present paper.

2. Experimental study

2.1. Experimental procedure

The sample was prepared in an ultrahigh-vacuum system (10^{-10} Torr) with a set of surface preparation and characterization facilities: LEED, AES and STM. The surface of the Ag single-crystal used was mechanically and chemically polished and presented a [001] orientation (to within 0.1° as checked by X-rays diffraction). The surface preparation consisted of a clean-up of the surface by repeated cycles of sputtering with Ar^+ ions (around 500 eV), followed by extended annealing at 500 °C for a few minutes to get a sharp (1 × 1) LEED pattern. Using a calibrated Knudsen cell, 0.5 Ge ML have then been deposited at room temperature and the $p(2\sqrt{2} \times 4\sqrt{2})R45^\circ$ superstructure has been checked by LEED and STM. The dissolution process of this superstructure has been characterized by STM at room temperature after a first annealing at 260 °C for 5 min and after a second one, still at 260 °C but for 20 min more.

2.2. STM images

The STM images presented in this paper have been recorded before and after various stages of the dissolution process of Ge on Ag(001). The initial conditions of the experiment are illustrated by images recorded after the deposition at room temperature of 0.5 ML Ge (Fig. 1a) which shows in one direction wavy rows of white spots assigned to small clusters of Ge. These clusters correspond to four Ge atoms (tetramers) as can be seen in Fig. 1b in which atomic resolution has been achieved. The unit cell of the $p(2\sqrt{2} \times 4\sqrt{2})R45^\circ$ superstructure is drawn on both STM images. Let us recall that a previous SXRD study [7] has shown that Ge tetramers are located in adatom positions on the Ag surface, three being in hollow sites and the fourth near a bridge position.

Fig. 2 shows the same surface after about 5 min annealing of the sample at 260 °C. The signature of the dissolution in these images is the appearance of a set of black squares, attributed to Ge tetramer vacancies, which are not randomly distributed on the surface but are locally ordered on two or three periods only. We have drawn in Fig. 2b the two ordered structures of vacancies (L1 and L2) observed after this short annealing. An STM image

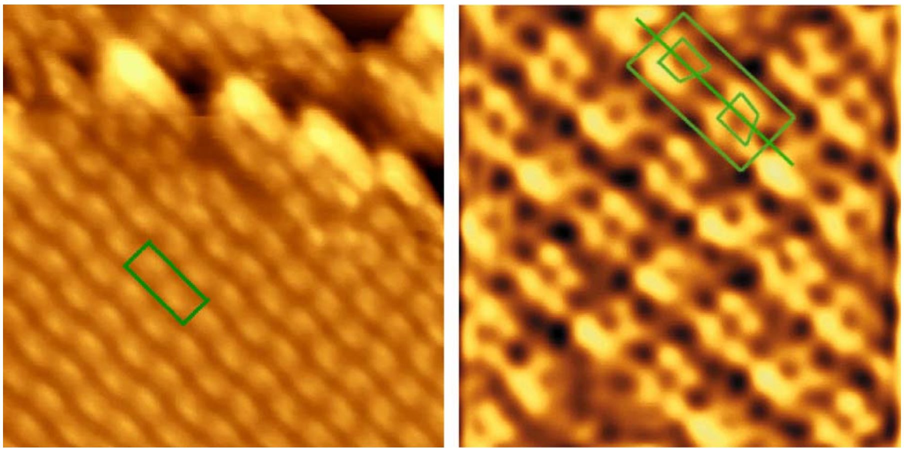


Fig. 1. (a) Filled-state STM image of the Ag(001) surface recorded at room temperature after the deposition at room temperature of 0.5 ML Ge (10 × 10 nm^2, $V = -1.7$ V, $I = 1.6$ nA), (b) filled-state STM image atomically resolved (4 × 4 nm^2, $V = 0.004$ V, $I = 8.6$ nA).

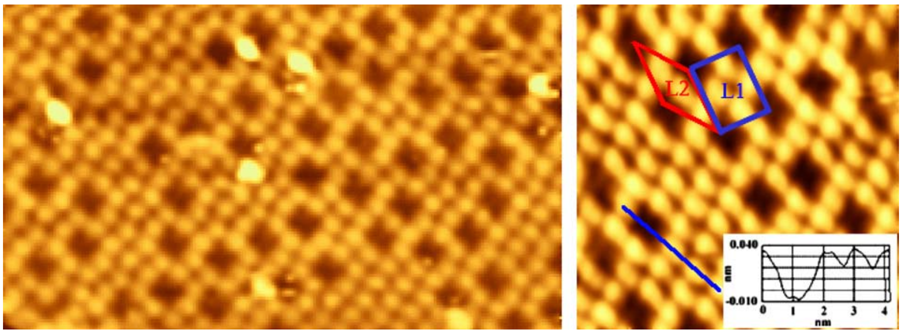


Fig. 2. Filled-state STM images of the Ag(001) surface recorded at room temperature after a short annealing of the sample at 260 °C for about 5 min. (a) 20 × 11 nm^2 area ($V = -1.5$ V, $I = 1.5$ nA), (b) 10 × 10 nm^2 area ($V = -1.7$ V, $I = 1.0$ nA).

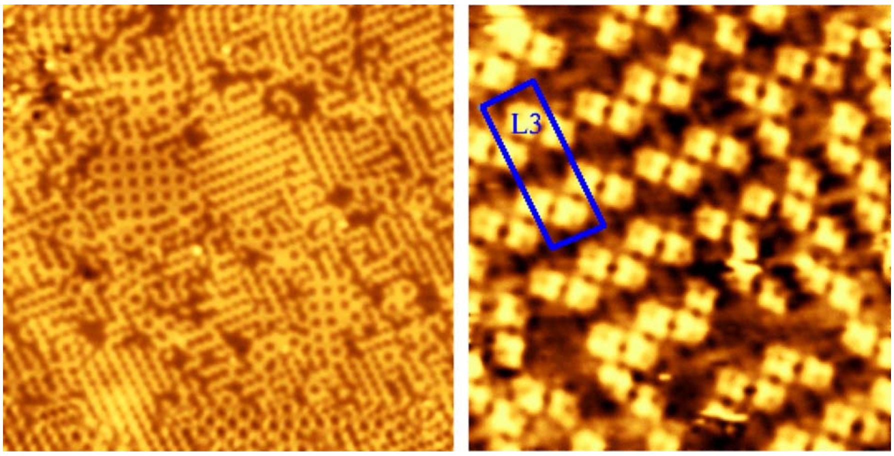


Fig. 3. Filled-state STM images of the surface recorded after a further annealing of the sample for about 20 min still at 260 °C. (a) 50 × 50 nm^2 area ($V = -0.05$ V, $I = 3.7$ nA), (b) 10 × 10 nm^2 area ($V = -0.07$ V, $I = 3.4$ nA).

of the surface recorded after further 20 min of annealing of the sample still at 260 °C in Fig. 3a, shows a prominence of the dissolution effect. One now observes not only the same square structure (L1) as in Fig. 2b but also a new one (labeled L3 in Fig. 3b) with a zigzag-like shape. A magnification of a part of these domains is reported in Fig. 3b revealing the details of this new arrangement of tetramer vacancies.

2.3. Analysis of the data

The first interesting point of this set of observations is the confirmation that the existence of a plateau on a dissolution kinetics recorded by AES [6] indeed corresponds to a specific surface structure. In this case, the absence of LEED pattern at the end of the kinetics was due to the size domains of these arrangements of tetramer vacancies which are too small to give rise to a strong coherent signal. The second and striking point is the absence of Ge trimers and dimers after the dissolution process. More precisely only monomers (isolated atoms) are observed in some tetramer vacancies as it can be seen in the lower part of Fig. 1b. The Ge dissolution proceeds by successive disappearance of complete Ge tetramers, which confirms the large stability of the latter on the Ag(001) surface. Because the dissolution of a complete tetramer directly in the bulk is highly unlikely, one can imagine that the dissolution begins by that of the first Ge atom which leaves a trimer on the surface. This trimer being less stable, each Ge atom can then either diffuse also quickly into the bulk, after a rapid surface diffusion, or attach to another incomplete tetramer. Concerning the atomic mechanism of dissolution, the line scan through a tetramer vacancy (inset of Fig. 2b) shows a corrugation of about 0.04 nm. Since the corrugation of isolated Ge tetramer on Ag(001) is close to this value (in similar recording conditions) one can conclude that there is no Ag atom inside these tetramer vacancies. This suggests that the first stage of the dissolution process is not an exchange between a Ag atom and a Ge one but more probably an atom-vacancy mechanism as it is the case for the Ge bulk diffusion in Ag [8]. Finally, the third interesting point concerns the different structures of tetramer vacancies which appear as a peculiar and novel ordered surface pavement, signature of repulsive interactions between these tetramer vacancies (or equivalently between tetramers). In that sense, one can speak of self-organization of Ge tetramers, as resulting of a spontaneous 2D realization of these interactions. This is the balance between these interactions which will be discussed hereafter.

3. Theoretical study

3.1. Lattice gas analysis

We will not discuss here the apparent enhanced stability of Ge tetramers with respect to the other Ge_n clusters, but we will try to identify the nature of tetramer–tetramer interaction which could explain the ordered tetramer structures observed in the previous STM images. Indeed, it is known that dissolution blocking on such surface alloys is only possible if they are linked to at least metastable ordered compounds [2,3]. Therefore, the pavements displayed in Figs. 1–3 can be considered as an experimental evidence of the existence of short-range repulsive interactions between Ge tetramers which tend to order them in a specific (and unusual) way. The aim of this section is to develop a semi-phenomenological method to get some insight into the hierarchy of the different interaction energies which lead to the formation and stability of the observed novel structures. Indeed, the various superstructures adopted by the Ge vacancies can be rationalized by simplifying their description which can be achieved by replacing Ge tetramers by individual entities, which means that one neglects their slight internal asymmetries. Note that such a simplified description of Ge tetramers in terms of quasiparticles is at the moment only grounded on the previous experimental observations along which tetramers are indeed the individual pieces of the puzzle, from the initial steps of its growth (isolated tetramers) to its dissolution (which proceeds by successive disappearance of these tetramers). Such a change in scale of the description should be completed from the theoretical point of view by energetic (ab initio) calculations confirming the enhanced stability of these tetramers. This will be a future step of the study but is not necessary here since our goal is just to rationalize our experimental observations. Doing that, every structure observed during dissolution (the L1, L2 and L3 structures) can be described within a lattice gas analysis (tetramer quasiparticles Ge_4 versus tetramer vacancies Vac_4) on a square 2D lattice as illustrated in Fig. 4a–c.

The first striking feature which appears from the figure is that these ordered superstructures are not the ones usually observed at either the same (Fig. 4d) or other (Fig. 4e) concentrations for a standard set of interactions between the particles dominated by those (repulsive) between first neighbours, the other ones being usually strongly and monotonically damped by distance [9,10]. In other words, the tendency to ordering in a A–B system (A and B referring to different species: two elements, element and vacancy,...) is generally driven by strong short-range repulsive interactions which forbid (as much as possible) A and B to occupy first neighbour positions. The arrangement of the equilibrium ordered structure is then the one which maximizes the number of A–B pairs, as it is the case for the so-called usual 2D structures displayed in Fig. 4d and e. In order to get more insight on this surprising behaviour, it is tempting to analyse the energetic of the system within an Ising-like description, as usually done and justified even for more complex interactions when one is only interested in ordering phenomena [2].

3.2. Derivation of pair interactions

In this Ising-like model the energy of a given configuration, at a given vacancy concentration (c), can be written as

$$E = E(c) + \sum_n p_n p_m V_{nm} \tag{1}$$

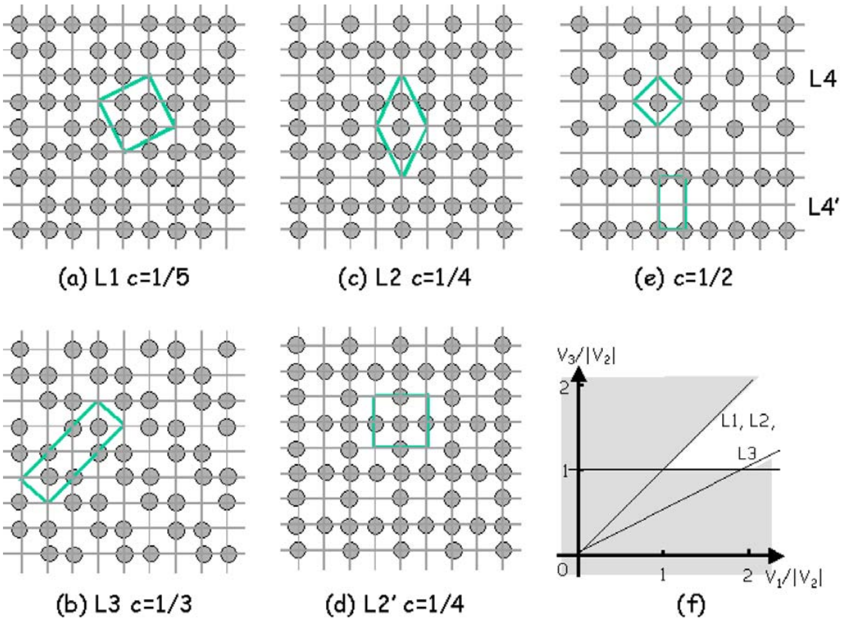
in which p_n is a so-called occupation number which is equal to 1 or 0 depending on that a site n of the square lattice is occupied by a vacancy or a quasiparticle (tetramer entity), V_{nm} are the effective interactions between vacancies at sites n and m, resulting from the Ge–Ge and Ge–Ag actual ones, and $E(c)$ a constant which only depends on concentration. Let us note that in such a lattice gas analysis, the effective interactions V_{nm} is a linear combination of the interactions between the quasiparticles (Ge_4 and Vac_4):

$$V_{nm} = \frac{V_{nm}\mathrm{Ge_4Ge_4} + V_{nm}\mathrm{Vac_4Vac_4} - 2V_{nm}\mathrm{Ge_4Vac_4}}{2} \tag{2}$$

This means that it is completely equivalent here to speak of interactions between vacancies or between Ge tetramers, to describe the ordering process. In this framework, we will limit the set of interactions as a function of distance to the minimal set which allows us to discriminate all the competitive structures. This leads us to neglect the interactions beyond third neighbours, i.e. only $V_1, V_2, V_3 \neq 0$. In this framework, the occurrence of L1, L2 and L3 structures instead of L2', L4 and L4' ones, leads to a set of inequalities which can be synthesized as (see Fig. 4f)

$$2V_3 > V_1 > V_3 > |V_2| > 0 \tag{3}$$

which translates into strong repulsive interactions between tetramer vacancies which forbid them to be first or third



(a) L1 c=1/5 (c) L2 c=1/4 (e) c=1/2

(b) L3 c=1/3 (d) L2' c=1/4 (f)

Fig. 4. Schematic description of the 2D vacancy ordered structures experimentally observed (a–c) or which could have been expected (d–e). Synthetic diagram of the Eq. (2) (f).

neighbours, the interaction being weaker and of no definite sign in second neighbour positions. Obviously, one can wonder in view of this sequence if the cut-off at the third neighbour is still justified or if the introduction of non-zero V_4 could modify the results of Fig. 4f. The answer is that, cutting the interactions beyond the ones necessary to discriminate the competing structures, here beyond V_3, means that the latter can be viewed as possibly renormalized by longer distance neglected interactions (essentially V_4, the next ones being far beyond). Taking into account that V_1 remains larger than V_3 and that the number of third neighbours is twice that of fourth ones, one can expect the correction to be negligible. Therefore our main result, namely that V_3 is stronger than V_2 and of the same order of magnitude as V_1 would remain unchanged. The origin of this rather unusual behaviour has to be found in both the nature of the chemical bonding which has to combine metallic and semiconductor characteristics, and the relaxation of the stress induced by epitaxy [11–13]. Let us note however that, according to previous works devoted to elastic interactions [14,15] there exists a strong elastic anisotropy at the surface. More precisely, in the peculiar case of Ag, the elastic interactions between square lattice domains are expected to be attractive in the $\langle 100 \rangle$ direction [15,16], which is not the case here. Even though the situation here is probably more complex, due to the strong Ge–Ag interaction, this seems to indicate that the puzzling sequence of interactions displayed in Eq. 3 more probably originates from chemical bonding than from stress relaxation. The latter argument seems to be confirmed by noticing that a somewhat similar reversal of the sequence of the interactions with respect to distance has already been observed for 3D vacancy ordering in sub-stoichiometric transition metal carbides [17]. In that case, the observed 3D ordered structures between carbon atoms and vacancies were explained by effective interactions between vacancies (mediated by the metal sublattice), such as $V_2 > V_1 > 0$, which was confirmed by tight-binding calculations [18]. In order to confirm the sequence observed in the present case, one should perform similar calculations of the interactions using either tight-binding or ab initio calculations to calculate the energetic balance between two situations in which the vacancies are, respectively, isolated and in position of *n*th neighbours. Such calculations, which require very large simulation cells to properly account for stress relaxation with large unit cells, are under progress.

4. Conclusion

To summarize, we have presented here an STM study of dissolution of Ge/Ag(001) which shows that it proceeds by successive disappearance of tetramer entities. Moreover, it has allowed us to assign the successive slowing down of the kinetics reported during this dissolution to the formation of ordered 2D arrangements (pavements) of tetramer vacancies. A lattice gas analysis of the latter reveals a very unusual sequence of pair interactions between these vacancies, probably mediated by the substrate. The origin of this rather unusual behaviour has probably to be found in the nature of the chemical bonding which has to combine metallic and semiconductor characteristics, the effect of stress relaxation being more complex to predict here. From a more applied point of view, this means that playing on both chemical bonding and size-mismatch stress release, one could design ad hoc templates which could then be used to organize adsorption of molecules or metals in view of reaching specific properties.

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