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Spinodal decomposition driven formation of Pt-nanowires on Ge(001)

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Abstract

Using low energy electron microscopy, we have found that the deposition of Pt on Ge(001) leads to the formation of a surface confined eutectic liquid when the system is heated above 980 K. From the bulk phase diagram we derive the composition of the eutectic phase: $\text{Ge}_{0.78}\text{Pt}_{0.22}$. Upon solidification and further cooling down, two distinct types of terrace emerge, the so-called α and β terraces, which have been assigned previously as relatively Pt-poor and Pt-rich, respectively. Immediately after solidification β terraces fully cover the surface, while further cooling leads to their partial transformation into α terraces. Subsequently, Pt nanowire domains nucleate and grow exclusively on β terraces at about 600 K. The results are discussed using spinodal decomposition concepts and reveal a new pathway for nanowire formation.

Keywords: nanowires, germanium, low energy electron microscopy

1. Introduction

The formation of eutectics and their properties is a current topic in surface physics and nanotechnology. Because of its importance to the semiconductor industry, as well as its nanotechnological applications, the AuSi system has attracted special attention. The $\text{Au}_{0.82}\text{Si}_{0.18}$ alloy has a eutectic temperature of about 632 K, i.e. far below the bulk melting temperatures of



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both Au (1337 K) and Si (1687 K). Eutectics play an important role not only in technology through e.g. soldering, but also in nanotechnology. An intriguing example of the latter is the growth of semiconducting nanowires. Wagner and Ellis [1] introduced their so called vapor–liquid–solid (VLS) method. They took a suitable substrate with some droplets of gold. When this system is exposed to a Si-containing gas at sufficiently high temperature, the gas decomposes and a AuSi eutectic droplet is formed. Further exposure to the Si-containing gas leads to an increase of the Si content and finally to supersaturation and the precipitation of Si below the droplet, whilst the eutectic droplet continues to reside on top. As a result Si nanowires will grow from the substrate into vacuum with a typical diameter of a few nanometers [2]. It is emphasized that these perpendicular nanowires only grow when the temperature is (slightly) above the eutectic point.

Inspired by publications by Shpyrko *et al* [3, 4], Pinardi *et al* [5] were able to produce a Au–Si eutectic on clean silicon. For this purpose a relatively thick (3 nm) layer of Au was deposited on Si(001) and the system was heated subsequently. Their experiments show that it is possible to obtain a (near) surface confined eutectic with a bulk-like composition on top of a pure Si substrate. The eutectic point is at 632 K with the melting points for gold and silicon at 1337 K and 1687 K, respectively. The main finding of the latter paper is the presence of an ordered surface layer (a frozen layer) on top of the eutectic liquid as opposed to surface melting. This may be related to the extremely deep eutectic point, compared to the $\text{Ge}_{0.78}\text{Pt}_{0.22}$ eutectic that is the topic of this study, and where the bulk eutectic point is at 1045 K with melting points of 1211 K and 2041 K for Ge and Pt, respectively.

According to textbook physics the system will show segregation during cool down from the eutectic point and it will strive for coexistence of the two nearest stable phases. For the GePt eutectic these would be pure Ge and Ge_2Pt . The process of demixing is called spinodal decomposition. We stress that there could be strong surface effects. It is already clear from the Pinardi experiments that the eutectic conditions are not necessarily reached for the total crystal volume, but can be restricted to a number of layers near the surface. We will refer to this as a surface confined eutectic. In this case the eutectic separates upon cooling in components, which are seen as isolated islands [5]. Finally, we note that the surface may not only give rise to slightly different eutectic compositions, but may also form stable phases that are different from the bulk, for instance caused by surface reconstructions.

Here we report on an *in situ*, real-time study of the nanowire formation in the GePt system using low energy electron microscopy. This specific information is not available from earlier studies. Pt nanowires have been shown to be a result of an anneal of the Pt-covered Ge(001) surface above 1050 K. Two distinctly different terraces are observed, which were referred to as α and β terraces [6–8]. Defect free, μm long and one atom wide Pt nanowires grow [9–14] only on the Pt-rich β terraces. In what follows we will discuss the new observations. In short, we find a surface confined eutectic that plays a crucial role in the formation of the Pt nanowires. However, compared to the VLS method this happens with an entirely different twist: during cooling down from the eutectic point nanowires are formed that are oriented parallel to the surface rather than perpendicular. The VLS grown, perpendicular nanowires only emerge with the liquid temperature above the eutectic point, as the result of supersaturation and precipitation of the nanowire material from the eutectic liquid. In contrast, the current Pt nanowires grow parallel to the Ge(001) surface, precipitation occurs far (about 350 K) below the eutectic point, and kinetic limitations play a decisive role. Finally, we emphasize that the origin of the Pt wires

on Ge(001) is quite different from that of the Au-induced nanowires on Ge(001) [15, 16], which was recently discussed in terms of a wetting-dewetting transition [17].

2. Experimental procedure

The experiments were performed in an Elmitec LEEM III microscope with a base pressure of 5×10^{-11} mbar. The Ge(001) substrate with a size of $10 \times 10 \times 0.5 \text{ mm}^3$ was cut from a nominally flat (miscut less than 0.3°), single-side-polished n-type wafer. During the experiment, the sample was mounted on a Mo holder. We carefully prevented it from making contact with any other metal. The sample was cleaned by cycles of sputtering with 600 eV Ar^+ ions, followed by short annealing through e-beam bombardment of the Mo base plate up to 750 K. After several cleaning cycles, an atomically clean Ge(001) surface exhibiting a well-ordered double domain (2×1) LEED pattern [22] was obtained. Pt was evaporated by heating a 99.997% purity Pt wire wrapped around a tungsten filament.

3. Results and discussion

We begin our experimental observations with the real-space LEEM image of figure 1(a). Pt was deposited on the Ge(001) substrate at room temperature up to an equivalent coverage in excess of 1 ML. At a temperature of 985 K, we observe no clear structural features like steps and kinks which are normally associated with a solid crystalline surface. The corresponding LEED pattern, shown in figure 1(b), consists of a diffusely scattered contribution, supplemented by secondary electrons. We explain both our real and reciprocal space observations by the formation of a surface confined eutectic. From consulting the bulk GePt phase diagram, partially plotted in figure 2, we conclude that the composition corresponds to 22 atomic percent Pt. Although the absence of structural features and a LEED pattern is by no means a conclusive indication of surface melting, this is further evidenced from the temperature-dependent profiles of the (00) LEED spot shown in figure 1(e). Moreover, when the substrate is allowed to slightly cool to 976 K, as shown in figure 1(c), atomic steps reappear, and the terraces have a homogeneous appearance with little-to-no contrast variations. This solidification of the surface molten layer becomes more evident if we consider the μ LEED pattern of the surface obtained at 963 K, immediately after its solidification. Figure 1(d) shows this well-ordered (1×2) pattern of one of the single domains shown in figure 1(c). Later on, we will argue that this pattern can be attributed to the previously introduced β phase [9].

Figure 3(a) shows that shortly after the solidification, a second phase with a higher brightness nucleates at the previously formed atomic steps. Upon slowly cooling, it expands to occupy the visible surface area, as shown in figure 3(b), and coincides with the formation of several small bright features. The structure of this second, brighter phase could also be resolved using μ LEED. Figure 3(c) shows the μ LEED pattern of a few small domains of this second phase. It corresponds to the so-called α phase, described as the usual dimer-reconstructed Ge(001) surface containing a much higher amount of missing dimer defects and adatoms [9, 11].

The formation of a surface confined eutectic provides a perfect framework to explain the emergence and evolution of the α and the β phases below the eutectic point. The bulk eutectic corresponds to $\text{Ge}_{0.78}\text{Pt}_{0.22}$ at 1045 K. We find it to occur at about 980 K, which is a first indication for the importance of surface effects. Cooling down gives rise to spinodal

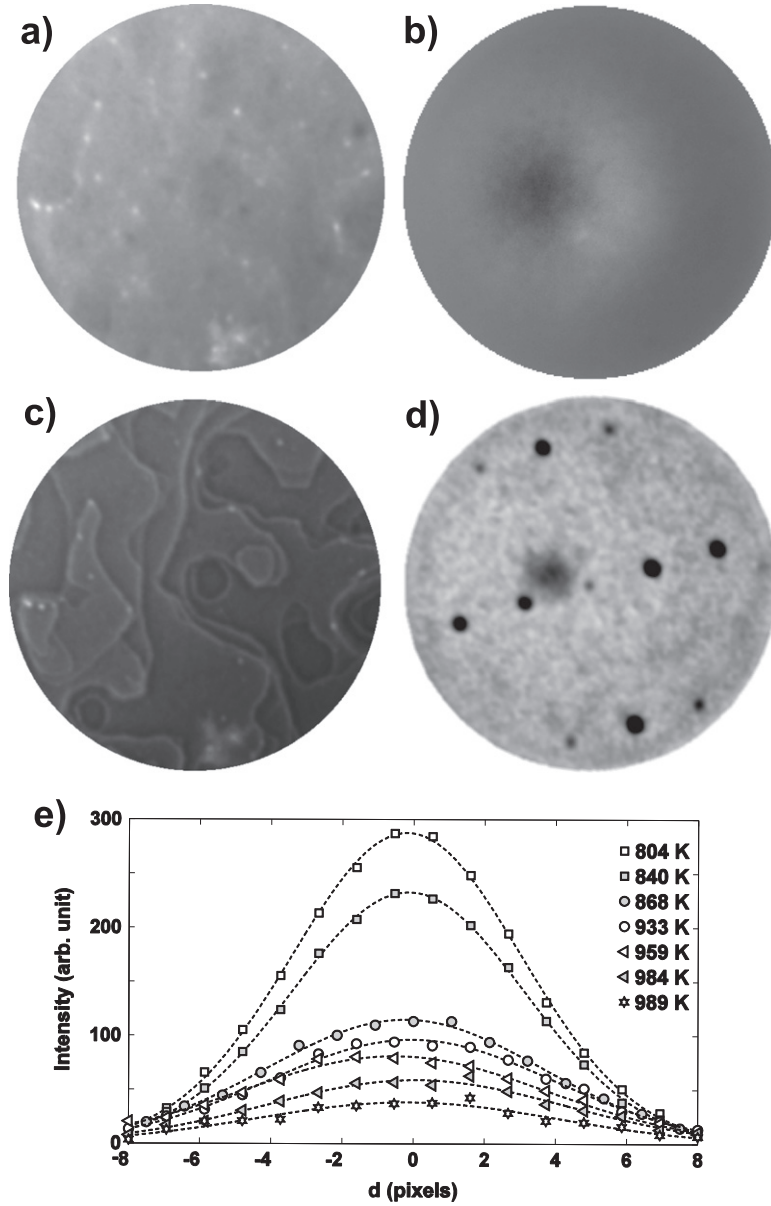


Figure 1. (a) A $10\ \mu\text{m}$ field-of-view (FOV) bright-field LEEM image of a molten Pt–Ge surface alloy at 985 K. The surface is featureless, with some protrusions from the underlying solid substrate still visible. (b) The diffuse LEED pattern of this surface, recorded at 1009 K with an electron energy of 14.0 eV. The slight asymmetric appearance of the pattern results from the secondary electron (SE) contribution. A two-dimensional (2D) Gaussian was fitted to the SE signal and then subtracted from the original pattern. (c) A $10\ \mu\text{m}$ FOV bright-field LEEM image of the just-solidified surface at 976 K. Bright lines are atomic steps, and the gray areas are the β phase domains. (d) The μLEED pattern of one of the β phase domains shown in panel (c), recorded at 963 K with an electron energy of 16.8 eV using a $1.4\ \mu\text{m}$ field-limiting aperture. (e) The temperature-dependent cross-section profiles of the (00) LEED spot during heating. The dotted lines are the Gaussian fits to the original intensities of the (00) spot at each temperature. k_x is the parallel component of the wave vector change.

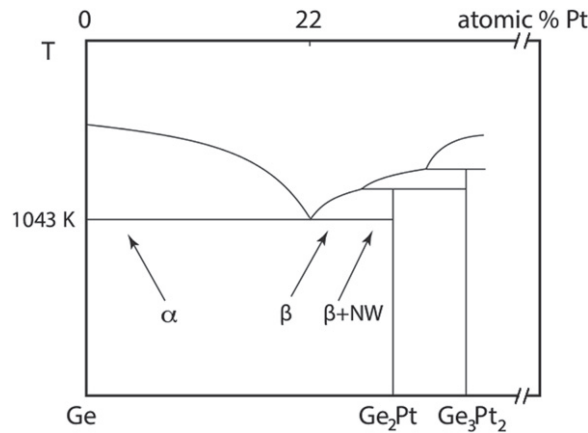


Figure 2. Partial bulk phase diagram of the Pt–Ge binary alloy system [18]. A eutectic is found at a composition of 22 atomic percent Pt.

decomposition into the nearest stable compounds. For the bulk case these would be pure Ge and Ge_2Pt . Actually, we interpret the formation of small 3D excretions, visible in figures 3(b) and 4, as Ge_2Pt crystallites. The latter situation is similar to the AuSi case, where stable 3D crystallites are also formed after cooling down [5, 19–21]. Although the bulk situation provides a good starting point to understand the system, we stress that surface effects inherently complicate the situation. This might go as far as depth dependent equilibrium compositions, which we neglect here: Pt is dissolved in near surface layers [23]. Complications certainly arise, most directly through dimer formation at the surface, which tends to stabilize the surfaces and occurs in both the α -phase and the β -phase. As a consequence it may well be that the β -phase is the most stable phase at the Pt-rich side of the eutectic composition. Segregation of Ge to the pure substrate at its interface with the eutectic should be an active process at 980 K [24]. So one should expect the β phase, with its suggested 25% atomic Pt concentration [9], to appear first, in agreement with the observations of figure 1(c). The thickness of the solidified Ge–Pt mix is believed to decrease simultaneously, but we have no access to this information. The completion of the segregation requires sufficient mobility and kinetic effects may become important at lower temperatures. The α phase may be relatively stable and act as the preferred (metastable?) structure on the Pt-poor side of the eutectic composition, when precipitation of Ge at the interface becomes kinetically hampered due to cooling or larger diffusion distances. The small Ge_2Pt crystallites are still believed to be preferred receptors of excess Pt, but diffusion limitations may be significant, especially when the temperature is lowered further. The excess Pt from the cooling thin film is then repelled from the decomposing GePt mixture towards the β terraces where it forms the relatively stable Pt nanowires at about 600 K. The total Pt-concentration on these terraces (β + nanowires) corresponds nominally to the Ge_3Pt_2 compound in the GePt bulk phase diagram, which we consider as circumstantial evidence for our assignment. Further support for the importance of kinetic effects in the formation of the Pt-nanowires on the β terraces is the fact that their integrated size depends strongly on the cooling rate and becomes larger at higher rates.

From the model thoughts above, we conclude a distinct tendency towards decomposition in α terraces and Ge_2Pt crystallites and this we hold responsible for the partial decomposition of the β terraces during slightly later stages of the spinodal decomposition. Unfortunately,

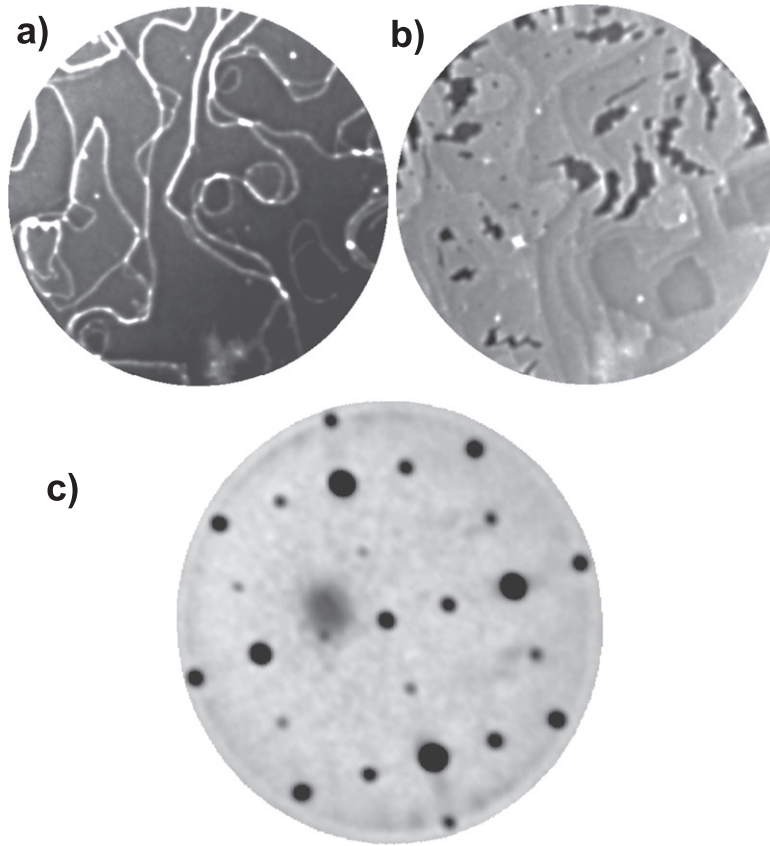


Figure 3. 10 μm FOV bright-field LEEM images of the nucleation and growth of the α phase on the Ge(001) surface, recorded with an electron energy of 1.1 eV during a slow cooling from high temperature. (a) The nucleation of the α phase, the bright rims, at 964 K occurs at the steps of the β terraces, see figure 1(c). (b) Further slow cooling to 705 K leads to the configuration visible in panel (b). The α domains have expanded and replaced β domains, the dark-gray areas. The bright spots in the image exhibit a focusing behavior which is characteristic for three-dimensional (3D) features. (c) The μLEED pattern of the α phase recorded at 377 K with an electron energy of 22.4 eV. A few small β domains were included within the 1.4 μm field-limiting aperture used for μLEED .

measuring the growth of the 3D crystallites is impossible due to their small size and field distortion effects that are inherent to LEEM. We cannot exclude that the α terraces constitute a metastable state compared to the possibly global equilibrium of clean Ge terraces.

The picture that we have developed is admittedly, and necessarily, somewhat speculative. This is mainly due to the fact that detailed information on the composition of the layers as a function of depth is not dynamically accessible in a spatially resolved manner with presently available techniques. Still, we consider the conceptual ideas outlined above as a plausible way of rationalizing our observations.

We now discuss a few more aspects of the nanowire covering of the β terraces. The α phase gradually expands at the expense of the β phase. If the surface is cooled sufficiently fast to approximately 600 K, the remaining β domains are converted into the Pt-induced nanowire domains. Figure 5(a) shows the first nucleation of a nanowire domain, the darkest of three

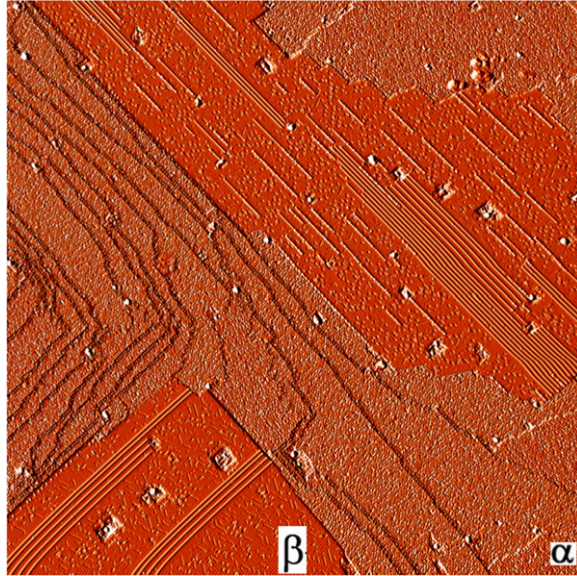


Figure 4. A scanning tunneling microscope (STM) image of size $200 \times 200 \text{ nm}^2$ recorded at room temperature (the bias voltage was -1.5 V , and the tunneling current was 0.5 nA). Some 3D clusters are visible within the α and β terraces. This can be due to the dealloying of a portion of the β phase into the α phase and some 3D clusters of probably Ge_2Pt composition, based on the bulk GePt phase diagram. It is also seen that the nanowires are terminated where they meet some 3D clusters or defects, and the edges of the nanowire patches are straight.

phases, within a β domain, left after a rapid cooling from the surface melting temperature. Later on, as shown in figure 5(b), more nanowire domains nucleate within different β domains at different times, and then, as illustrated in figure 5(c), grow further up to a size that is always limited by the size of the β domains. Figure 5(d) gives the $c(4 \times 2)$ μLEED pattern of one of the nanowire domains in figure 5(c), reconfirming the $c(4 \times 2)$ periodicity observed in previous STM measurements [9–12].

It should be noted here that, no matter how slowly the surface is cooled at this temperature range, the nanowire domains stop growing within the β domains, possibly indicating a compositional threshold for the formation of the nanowires, i.e. if the local composition within the β domains is lower than a critical limit, the nanowire domains do not grow further when insufficient Pt is available in deeper layers to locally form the Pt-rich (33%) β -phase and nanowires. In other words, the Pt source gets exhausted. Another interesting observation in figure 4, confirmed by figure 5(c), is that the interfaces between the growing nanowire domains and their corresponding precursor β domains always remain straight. This suggests that the nanowire formation involves virtually no mass transport parallel to the substrate. However, the intensity of the $(\frac{1}{4}, 0)$ LEED spot shows some hysteresis during heating and cooling, reflecting that the nanowire formation involves mass transport. Mass transport is therefore anticipated to happen preferentially perpendicular to the substrate. These observations support the zipper-like mechanism put forward by Fischer *et al* [11]. Moreover, it can be inferred from figures 3(b) and 5(c) that the ratio of the surface covered by the nanowire domains can be tuned by adjusting the cooling rate of the system from the surface melting point. If we cool it rapidly, the meta-stable β phase domains do not have sufficient time to be converted into α domains. This leaves a surface

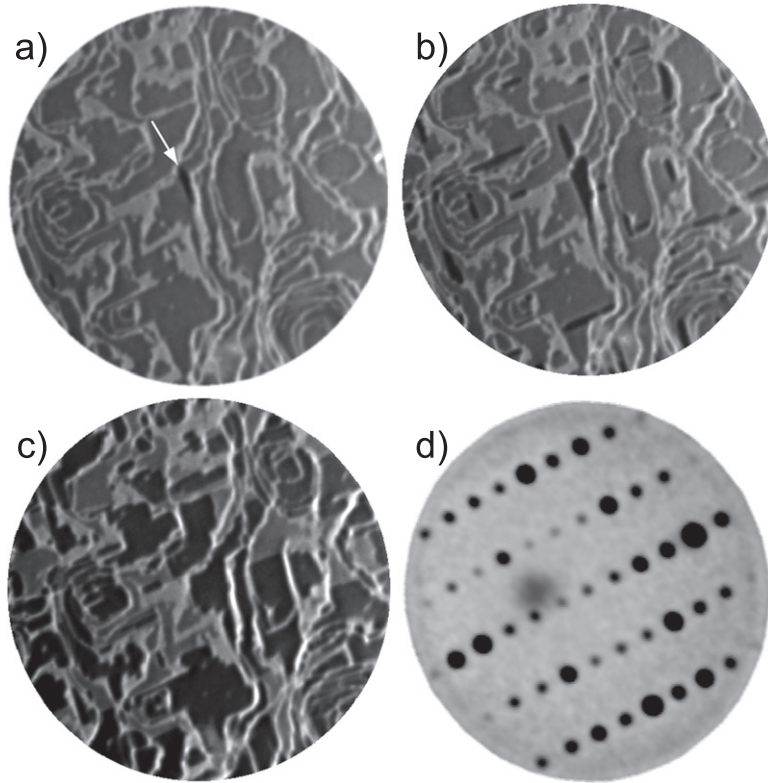


Figure 5. 10 μm FOV bright-field LEEM images of the nucleation and growth of the Pt-induced nanowire domains on the Ge(001) surface, recorded with an electron energy of 1.1 eV during cooling. The nanowire domains (darkest areas) nucleate at different temperatures from within different β phase domains (the dark-gray areas), and grow at the expense of the β domains. The temperatures in panels (a), which shows the nucleation of the first nanowire domain highlighted by the arrow (b), and (c) are respectively 621, 610, and 600 K. The light-gray areas are the alpha phase domains. Also shown in panel (d) is the $c(4\times 2)$ μLEED pattern of a single nanowire domain recorded at a temperature of 600 K and an electron energy of 20.1 eV.

mostly covered with β domains which are the precursor for the formation of the Pt nanowires. This also shows that both the α and β phases can be kinetically stabilized by cooling to room temperature.

4. Conclusions

In summary, we have reported a LEEM and μLEED study of the thermal history and temporal evolution of the three distinctly different types of terrace on Pt-modified Ge(001): the α terraces, the β terraces and, in particular, the β terraces covered with Pt nanowires. We have observed the emergence of a surface confined eutectic $\text{Ge}_{0.78}\text{Pt}_{0.22}$ with a eutectic point at 980 K. The spinodal decomposition of the eutectic upon cooling provides a straightforward framework to understand our observations of this complex system. The nearest stable bulk phases, clean Ge and Ge_2Pt are the natural recipients of excess Ge and excess Pt from both components of the mixture during spinodal decomposition. The presence of the surface complicates this course of

affairs since the dimerized α and β terraces may form (meta?) stable constituents. The Pt rich β terraces (Pt content of 25 atomic percent compared to a Pt concentration of 22% of the eutectic) form immediately after passing the eutectic point during cooling. We believe that a limited precipitation of Ge at the hidden mixture–substrate interface may be the reason for the delayed appearance of α terraces and the transformation of β - into α -terraces. We attribute the formation of the Pt nanowires on the β terraces to the lack of Pt mobility towards the 3D (probably Ge_2Pt) crystallites. The formation of Pt nanowires on the β terraces is certainly influenced by kinetic limitations: the faster the cooling, the larger the portion of the surface covered by the β terraces will be, eventually resulting in larger Pt nanowire domains. In this case excess Pt from deeper layers precipitates in support of the zipper-like formation mechanism for the Pt nanowires [11].

In recent years we must have prepared Pt nanowires on Ge(001) over one hundred times. Although we managed to prepare them at will, a few questions concerning their emergence remained unsolved until the present study. We varied several parameters like anneal temperature, the subsequent rate of cooling and the amount of deposited Pt over a wide range. We found that in order to produce the Pt nanowires we needed a minimum anneal temperature of about 1050 K. Also we tried very hard to cover the surface completely with nanowires, but failed rigorously. A third observation is an increase of the exposed fractional area of the nanowires on β terraces with increased cooling rate. With the current data and their evaluation at hand all pieces fall together. The required minimum temperature demonstrates that the eutectic is crucial for obtaining nanowires. The subsequent spinodal decomposition into stable phases with different composition necessarily leads to a heterogeneous surface and excludes the possibility of a homogeneous coverage of the surface with Pt nanowires. The dependence of the exposed area of the nanowires on the cooling rate reiterates the importance of kinetics. Any theoretical attempt to explain structure and composition of the nanowires therefore has to include thermal effects, both thermodynamic and kinetic, and a 0 K approach has no added value [25].

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