

## Formation of Ge–Pt Layer Compound on Pt(100)

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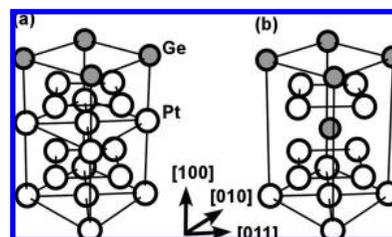
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We found a novel Ge–Pt layer compound on the Ge/Pt(100) surface by using alkali ion scattering spectroscopy (ALISS), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM). This surface alloy is produced after Ge deposition and annealing at 600 K, and explains the surprising apparent stability of a Ge adlayer on Pt(100) to very high temperature. At low Ge deposition amounts, Ge atoms form a  $c(2 \times 2)$  overlayer, but for deposition larger than 0.5 ML, excess Ge dissolves into the third layer in the  $c(2 \times 2)$  positions to form the ordered layer compound with excess Ge diffusing more deeply into the substrate.

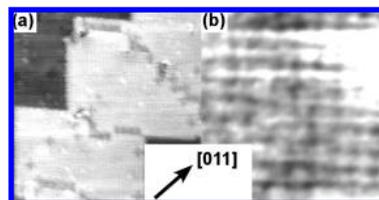
In our study of Ge deposition on Pt(100), we observed that annealing of more than 0.5 ML Ge above 600 K results in the formation of an ordered  $c(2 \times 2)$  Ge overlayer, with excess Ge dissolving into the Pt bulk. Annealing to 900–1200 K results in the formation of holes and eventually a percolating network of “channels” in the  $c(2 \times 2)$  Ge overlayer. Surprisingly, the  $c(2 \times 2)$  Ge overlayer remains on top of the Pt(100) surface up to the highest accessible annealing temperature of 900–1200 K, above which Ge desorption occurs. Such adlayer stability is surprising given the large number of bulk PtGe intermetallic compounds, the ready incorporation of Ge into the top Pt layer to make an ordered alloy on Pt (111), and the observation of diffusion of Ge in excess of 0.5 ML into the Pt(100) subsurface region. Herein, we present an explanation for this behavior, involving the formation of a  $Pt_2Ge$  surface alloy layer at a Pt(100) crystal surface.

Our observations are consistent with a simple intercalation of Ge atoms in alternate layers at a Pt(100) surface. Such self-assembly or compound formation bears on important problems in nanoscience and technology, such as self-assembled monolayers and quantum dots developed for easy surface fabrication at nearly atomic levels.<sup>1</sup> Layer compounds are one of the candidates for nano self-control materials.<sup>2</sup> They have mechanical anisotropy featuring stable cleavage planes parallel to the layer. Their electronic states show structural anisotropy, and vary with interactions within and between layers. They also change depending on the number of layers, and the control of layer compounds by one layer is important. To decrease the undesired defects, it is useful to intercalate heteroatoms without changing the lattice constant within the layer.

Experiments were performed in two ultrahigh vacuum (UHV) chambers. The clean Pt(100) surface was characterized by



**Figure 1.** Schematic drawing of the structure of Ge/Pt(100): (a)  $c(2 \times 2)$  Ge overlayer; (b)  $Pt_2Ge$  layered surface alloy.



**Figure 2.** STM topographs on Ge/Pt(100): (a)  $c(2 \times 2)$  Ge overlayer ( $18.3 \times 18.3 \text{ nm}^2$ ,  $V_s = -0.1 \text{ V}$ ,  $I_t = 0.29 \text{ nA}$ ); (b) amplified view of  $c(2 \times 2)$  Ge overlayer ( $3.3 \times 3.3 \text{ nm}^2$ ,  $V_s = -0.1 \text{ V}$ ,  $I_t = 0.29 \text{ nA}$ ).

scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS), X-ray photoelectron diffraction (XPD), and alkali ion scattering spectroscopy (ALISS).

We found a novel layer compound to be formed, which may have potential for nano fabrication in the Ge/Pt(100) system. This surface alloy can be produced by Ge evaporation and annealing at 600 K. Ge atoms form a  $c(2 \times 2)$  overlayer (Figure 1a) at 0.5 ML Ge deposition, and simply dissolve into the third layer in the  $c(2 \times 2)$  positions (Figure 1b) with increasing Ge dose to 1.5 ML. The STM images of the  $c(2 \times 2)$ -Ge/Pt(100) overlayer are displayed in Figure 2. The bright dots correspond to Ge atoms within the  $c(2 \times 2)$  structures. The evidence for Ge intercalation is revealed by  $Na^+$ -ISS and LEED. It is noteworthy that the step edges are along the Ge close packed directions.

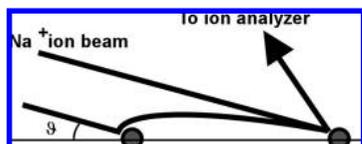
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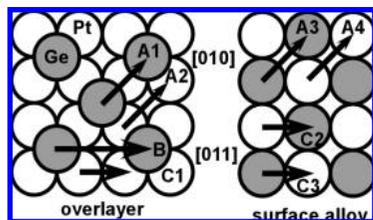
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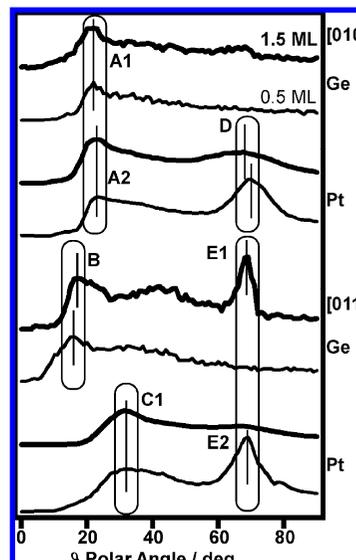
**Figure 3.** Schematic drawing of the mechanism of ISS polar scan at a surface.



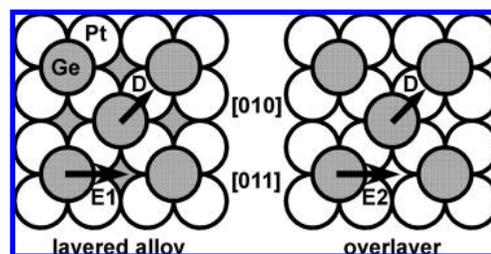
**Figure 4.** Schematic drawing for assignment of the overlayer and surface alloy structure by using ALISS scans.

The overlayer (Ge layer) and surface alloy (Ge–Pt mixed layer) is difficult to distinguish by STM because Ge is observed higher than the Pt atoms<sup>3</sup> due to chemical contrast.<sup>4</sup> Na<sup>+</sup>-ISS is a powerful technique to reveal the surface atomic structure.<sup>5</sup> Figure 3 gives a schematic drawing of the mechanism inherent to ISS polar angle scans. Na<sup>+</sup> ions are scattered along the conical shape called a shadow cone by neighbor atoms,<sup>6</sup> and scattered back to the analyzer. The scattering from distant atoms and atoms in the lower level gives peaks at a higher polar angle of  $\sim 70^\circ$ . The energy of the detected ions depends on the mass of the atom from which the ions are scattered back, and by combining this with the critical angle created by the shadow cone, both the element type and the position of the scattering atom in the surface can be determined. The approach used to distinguish between a  $c(2 \times 2)$  surface overlayer and surface alloy is shown in Figure 4. No difference in critical angle is expected along the [010] azimuth for scattering on Ge (A1 and A3) and Pt (A2 and A4). However, along the [011] azimuth, the critical angle for scattering on Ge is expected to be lower than that for Pt in the case of a Ge adlayer (B and C1) but will be the same as that for Pt in the case of a surface alloy (C2 and C3).

The ALISS results are shown in Figure 5. These spectra showed different polar angles of ISS peaks for Ge and Pt scattering along the [011] azimuth. This indicates that the Pt(100) surfaces after 0.5 or 1.5 ML Ge deposition and annealing at 600 K contain the  $c(2 \times 2)$  Ge overlayer, as depicted in Figure 1. The  $c(2 \times 2)$  LEED pattern was observed on both surfaces. The Pt-scattered peaks along the [010] azimuth at higher polar angles are attributed to the scattering from the second layer on both surfaces (D). On the other hand, the Ge- and Pt-scattered peaks along the [011] azimuth appeared around  $70^\circ$  and are attributed to the scattering from the third layer for 1.5 and 0.5 ML Ge deposited on the surface, as illustrated in Figure 6 (E1 and E2), respectively. These ALISS results indicate Ge exists in the first layer at 0.5 ML and in both the first and third layers for 1.5 ML Ge evaporation. The negligible Ge-scattered peak along [010] and the Pt-scattered peak along the [011] for 1.5 ML Ge evaporation around  $70^\circ$  might derive from the shadow cone made by the atoms in the second layer. These results indicate that the first and second layers are Ge and Pt layers, respectively, regardless of the existence of Ge atoms in the third layer on Ge/Pt(100). A small amount of Ge atoms may be present in the second layer as impurities, and Ge atoms in the third layer may be located around defects such as holes and step edges, as seen in Figure 2. These situations may explain the broad peaks observed around  $40^\circ$  along the [011] azimuth.



**Figure 5.** ISS polar scan of Ge and Pt scattered signals along the [010] and [011] azimuths. The vector between the atom making a shadow cone and the atom scattering back ion to analyzer is indicated. The layer assignment of both atoms is also designated.



**Figure 6.** Schematic drawing for assignment of the overlayer and the layered alloy with ISS polar scan.

The body-centered tetragonal Pt<sub>2</sub>Ge illustrated in Figure 1 is most plausible for 1.5 ML Ge deposition by analogy with the Si/Pt(100) surface.<sup>7</sup> The body-centered tetragonal Pt<sub>2</sub>Ge alloy does not exist as a bulk alloy structure, and thus is only produced as a surface length compound, reflecting the substrate structure strongly. The Pt layers of Si/Pt(100) rotate with respect to the substrate because of the  $\sim 7\%$  lattice mismatch, which could accelerate production of crystal boundaries. On the other hand, Ge/Pt(100) did not show such a rotation of the Pt layers. The Ge–Pt interaction is weaker than that for Si–Pt,<sup>8</sup> and the Pt<sub>2</sub>Ge layer can perhaps accommodate more strain at the Pt(100) substrate than for Si/Pt(100). Both Si and Ge atoms are much smaller than Pt atoms (15 and 12%, respectively), and this strain relief is considered to stabilize their layer structures. We can generalize that couples of heteroatoms with mild interaction and large lattice mismatch can form layer compounds without a drastic change of surface and subsurface morphology.

The STM topograph of Figure 2a showed that the step edges of Ge-covered Pt substrates are along the Ge close packed directions. This indicates that the  $c(2 \times 2)$  Ge overlayers are stable and control the step directions of the Pt substrate. When we take the layer structure and the step direction into account, the Ge/Pt(100) surface is considered to be on a complicated balance among the Ge–Pt, Ge–Ge, and Pt–Pt interactions.

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